PATHWAYS OF CHEMISTRY

VOL. II

D.P. GOEL

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PATHWAYS OF CHEMISTRY

VOL. II

(FOR CLASS XII)

2069

By

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Devotional offerings

to the lotus feet

of

His Holiness

Srimat Swami Bhuteshananda Maharajji

President

Ramakrishna Math and Ramakrishna Mission

Belur Math, Dist. Howrah, West Bengal

"Education is not the amount of information that is put into your brain and runs riot there, undigested, all your life. We must have life-building, man-making, and character-making assimilation of ideas."

—**Swami Vivekananda**

PREFACE

As we continue to teach, we continue to learn. We learn from our students as, each year, we help them in understanding their science courses. We also learn from our colleagues who have kindly offered many helpful suggestions in writing this book.

This book is designed for class XII students. It gathers together the requirements of the new syllabus introduced by the Central Board of Secondary Education, New Delhi. It takes into consideration not only the topics but the objectives set by the syllabus as well. It is an attempt to offer a simpler yet exhaustive exposition of the subject. It is an assurance to equip the students with all the informations on the topics.

In planning the book, the following general principles have been adopted :

— Each unit is prefaced with unit preview and a list of learning objectives. The purpose of the unit preview and learning objectives is to apprise the students of the scope of the unit.

— The subject matter has been presented in a sound, lucid and simple manner to help the students of all levels.

— The entire subject matter has been written in accordance with the recommendations made by the International Union of Pure and Applied Chemistry (IUPAC).

— Numerous illustrations and diagrams have been embodied in the text. These present most of the topics in visual terms.

— Throughout the book, the emphasis has been put on the use of SI units to explain the values of physical quantities.

— Many sovled numericals have been given to explain the subject matter and use of SI units.

— At the end of each unit, **'Self assessment questions'**, have been included. It is an integral part of the book. Hence, the subject matter is presented in an objective question-answer format with the dual purpose of providing the subject matter to the students in a crisp

form and of acquainting them with the possible questions on the matter.

— At the end of each unit, a collection of '**Terminal questions**' have been provided, which cover the whole unit and whose aim is not merely to test the reader's knowledge, but also to promote understanding and to stimulate further thought.

Care has been taken over the layout of each page so as to present the subject matter vividly and attractively using figures, graphs and tables to reinforce the text. The terminal questions at the end of each unit vary in style and these may be used in tests, in class-room discussions, in revisions or for home work.

Although considerable care has been taken in introducing the subject matter, yet the possibility of any error or ambiguity in matter/fact that may have found its way into the book in hand, cannot be ruled out.

In presenting the subject matter, I have kept in view the capacity and intelligence of an average student of class XII for which my daughter Medha a student of Class XII, Delhi Public School, Mathura Road, New Delhi-110003 presented a suitable model.

I hope that the students will discover the beauty of science as they advance through the units of the book and achieve their intended goal.

I look forward to the comments and suggestions from readers for improvement.

I sincerely thank our friends Dr. Mohan Katyal, Dr. (Mrs.) Rashmi Sachdeva, Mr. K.M. Mathew, Dr. Y.C. Sharma, Dr. V.B. Agrawal, Dr. M.C. Jain for their timely helps and suggestions.

I must thank Dr. S.C. Vats, Shri R.S. Goel, Smt. Satya Goel, Smt. Rajkumari Gupta, Shri P.K. Gupta, Shri Surya Prasad, Shri Sumer Chand Bansal and Shri Pavan Chaudhary for their constant encouragement in this humble endevour.

Finally, I must thank my wife and children for their patience, help and cooperation at all times.

D.P. Goel

Baisakhi Day, 1990.

CONTENTS

UNIT 1

Structure of Atoms and Molecules

Much of our knowledge about the internal structures of atoms has as its origin the fact that atoms are only able to lose energy in certain specific amounts, and that this energy can appear as light of particular colours.

UNIT PREVIEW

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Describe the wave properties of matter.
2. Describe the dual nature of electron.
3. Emphasize the introduction of de Broglie hypothesis.
4. State the restrictions placed on our ability to know the position and momentum of a small particle.
5. Explain the results of calculations from the wave mechanical model of the hydrogen atom in terms of orbitals and probable electron density.
6. List the four quantum numbers along with their possible values, and state their physical significance in terms of orbitals.
7. Draw shapes of orbitals.
8. Write the electronic configuration of elements.
9. Describe the molecular orbital theory for chemical bonding and its various aspects.
10. Explain how orbitals hybridize to produce a set of equivalent orbitals.
11. Explain the shapes of molecules on the basis of hybridization.

PART I

1.1. INTRODUCTION

You have already learnt that atoms are not the simplest forms of matter. They are composed of three fundamental particles, the electron, the proton and the neutron. The discovery of fundamental particles led to a modification of the Daltonian picture of an atom. It has helped to systematize chemical facts in ways that enhance our understanding of internal structure of atom. The discovery of electron had a strong bearing on the laws of classical physics (Newtonian mechanics) which were at one time, thought of as universal truth. It is now known that an atom consists of a small, heavy nucleus of protons and neutrons, and a surrounding region of space containing fast moving electrons.

When atoms react with each other, it is only their outer parts that ever come into contact. Therefore, since it is the electrons that occupy the outer regions of the atom, chemical similarities and differences must somehow be related to the way that the electrons are arranged. This arrangement of electrons is called the atom's electronic structure.

The observations that led to a gradual refinement and extension of the atomic theory are numerous indeed, a detailed description of some of them has been done in the earlier classes. We begin this unit with a discussion of the experimental facts that helped solve the mystery of electronic structure and led ultimately to the currently accepted concept.

1.2. DUAL—WAVE AND PARTICLE—NATURE OF MATTER AND RADIATION

At the beginning of the eighteenth century, there was an apparent conflict between the two theories describing the nature of light (electromagnetic radiation). Newton believed that a light beam is a stream of tiny particles and on the other hand Huygens suggested that light was a periodic wave disturbance. The wave theory received a better recognition as it could explain the interference and diffraction phenomena. Around the end of the nineteenth century certain experimental observations began to accumulate which could not be explained by the wave theory. All these observations had one thing in common—they were associated either with the way light is generated from other forms of energy or with what happens when light is absorbed by matter and converted into a different form of energy. The inability of the wave model to explain these observations revived the Newton's particle nature of light. This theory, developed by Max Planck and Albert Einstein, states that a light beam is a stream of quanta of energy, called *photons*. The energy (E) of each photon is proportional to the frequency (ν) of the light, *i.e.*,

$$E=h\nu$$

where h is a Planck's constant.

Photoelectric effect

This is a phenomenon which has stumpted the wave model. It could be successfully treated and explained by the photon model.

When a beam of light with a high frequency (or high energy) is allowed to fall on a metallic surface, it sets electrons in the metal into motion. These electrons can set up an electric current (Fig. 1.1). This phenomenon is known as the photoelectric effect and the emitted electrons are called photoelectrons.

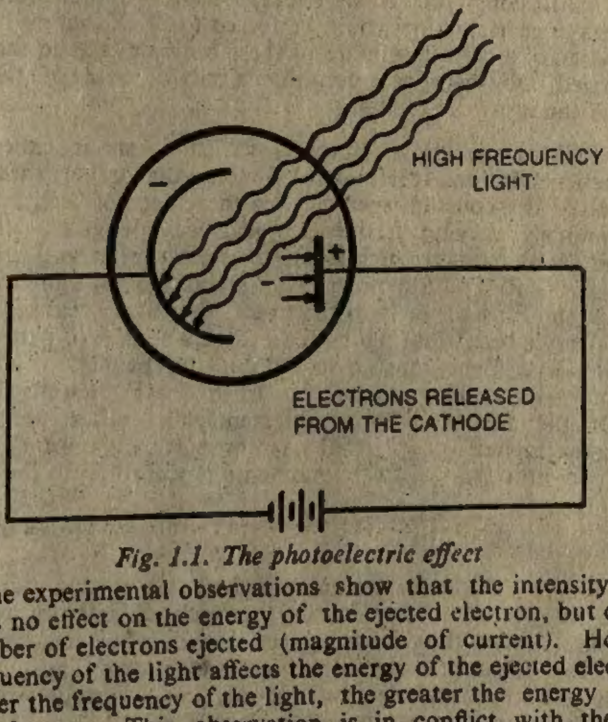

Fig. 1.1. The photoelectric effect

The experimental observations show that the intensity of the light has no effect on the energy of the ejected electron, but only on the number of electrons ejected (magnitude of current). However, the frequency of the light affects the energy of the ejected electron—the higher the frequency of the light, the greater the energy of the ejected electron. This observation is in conflict with the wave model, according to which the energy in a light beam depends on the intensity of the light but has no relation with its frequency.

The answer to these observations was given by Einstein in 1905; the light behaves as though it consists of particles, given the name **photons**.

According to the photon model, each absorbed photon gives all its energy, which is proportional to its frequency, to a single electron and this explains the photoelectric effect explicitly.

Matter waves

It has been widely held by atomic scientists that all physical events could be divided into two distinct and exclusive categories.

The first category included all events which could be characterized and described by the laws of the classical mechanics of motion of discrete particles of matter. The second category included all phenomena exhibiting continuous properties of waves.

Matter, as you know, is built up of discrete particles, and therefore, must occur in quantized amounts. Such objects are large enough to be readily observable. There are many other objects, however, that do not appear to be quantized, but otherwise seem to be continuous. But if we could see the fundamental particles that make up atoms, we would be forced to think that every object is composed of a certain number of these basic units, and therefore, is quantized. Objects appear continuous only because of the minuteness of the individual units.

Light, as we know, in all its varied forms is called electromagnetic radiation. It is a form of energy that travels through space as a wave at a constant speed, called the speed of light, possessing continuously varying frequencies and wave lengths. However, in explaining phenomena such as photo electric effect and black body radiation* which result from the interaction of light with matter, Planck and Einstein early in the twentieth century realised the need of Newton's belief that light consisted of a stream of particles. They showed that light must also exhibit the properties of matter by assuming quantized characteristics. In 1924, a French physicist, Louis de Broglie advanced the complementary hypothesis that all matter possesses (including a photon) wave properties, the wavelength being inversely proportional to the momentum according to the equation,

$$\lambda = \frac{h}{mv} \qquad (mv = \text{momentum})$$

Wave phenomena are not possible with visible particles with large momentum. Wavelengths for such objects are too small to measure. Under the circumstances, wave properties are apparent only for subatomic particles such as electrons. Thus, according to de Broglie's proposal electron should, under certain circumstances, show the properties pertaining to wave-like.

Experimental verification of wave nature of electron

If electrons have wave character, they must exhibit diffraction pattern, a property of waves. The first experimental demonstration of the wave nature of electron was provided by Clinton Davisson and Lester Germer (1927). They used a thin nickel crystal as the target element. The electron wavelength measured from diffraction

---

*A black body is consisted of oscillators of molecular dimensions, each with a fundamental vibration frequency, ν. Oscillators do not absorb or radiate energy continuously but only in discrete units called quanta ; and the energies absorbed or emitted must be whole number multiples of these quanta, *i.e.*, energy absorbed $= n\,h\,\nu$ where $n = 1, 2, 3, \ldots\ldots$ *etc.*, a quantum number.

pattern agreed exactly with the value obtained from the de Broglie's equation.

Estermann and Stern further verified the de Broglie hypothesis by diffracting helium atoms from a lithium fluoride crystal. It was also verified when Johnson of United States diffracted hydrogen atom from the same kind of crystal.

The de Broglie hypothesis was also verified by G.P. Thomson and J.J. Thomson in Britain, when they obtained excellent powder diffraction patterns by sending a beam of electrons through very thin sheets of various metals. Figure 1.2 shows a typical electron diffraction pattern produced by passing a beam of electrons through very thin aluminium foil. It is strikingly similar to the pattern obtained from diffraction of electromagnetic waves in the X-ray region, shown in Fig. 1.3. Subsequently, diffraction patterns were observed for other particles, such as neutrons, protons and even neutral atoms.

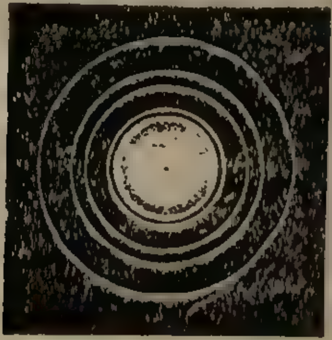

Fig 1.2. **Thomson's experiment :** *Diffraction pattern produced by passing a beam of fast moving electrons through thin aluminium foil. The foil consists of many tiny aluminium crystals. In each crystal the atoms are packed together so that there are many regular, parallel rows of atoms. These act like a set of parallel slits, and the electron waves passing through them give a diffraction pattern.*

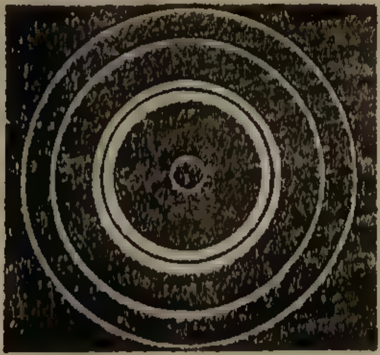

Fig. 1 3. **Thomson's experiment :** *Diffraction pattern produced by passing a beam of X-rays through metal foil.*

On the basis of mathematical calculation it has also been seen that the wavelength of a fast moving electron is in the *X*-ray region and is considerably shorter than that of visible light. Thus, the electron diffraction experiments provided enough support to

de Broglie's postulate of matter waves. Hence, 'particle' and 'wave' phenomena are not 'exclusive' but each class emphasises different attributes of all material processes. The particle aspect of matter is more significant in describing the properties of ordinary sized objects. The wave behaviour of matter is more significant in describing the characteristics of very small particle such as electrons, protons and atoms. Presumably everything in nature displays this basic duality. Electrons exhibit the interference phenomenon similar to light. Interference being a wave phenomenon, provides enough support to the wave-like behaviour of electrons.

1.3. WAVES AND PARTICLES

Almost everything in nature displays basic duality, *i.e.*, they possess the properties of both particles and waves.

A particle is specified by a mass, m, velocity, v, momentum, p, and energy, E. It occupies a definite position in space. Two or more particles in a given region of space maintain their individuality and do not interfere. A wave on the other hand is specified by its frequency, ν, wavelength, λ, *etc*. A wave is spread out, and occupies a relatively large region of space. Two waves present together tend to interfere (Fig. 1.4).

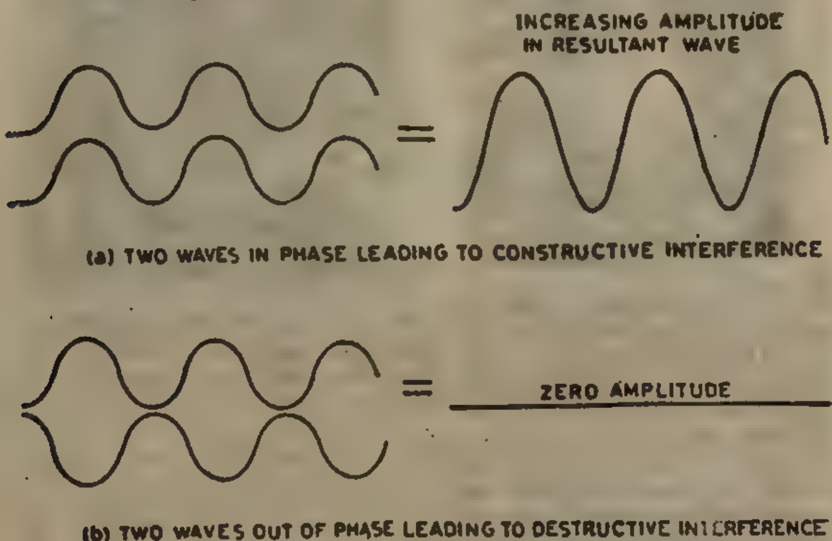

Fig. 1.4. Constructive and destructive interference.

There are five characteristic properties (Fig. 1.5) associated with any kind of wave, *i.e.*, wavelength, frequency, wave number, velocity and amplitude.

(*i*) **Wavelength.** It is the distance between any two successive crests (or troughs), *i.e.*, "points of equal displacement on successive waves". It is usually designated by the Greek letter lambda, λ, and

is measured in terms of Angstrom units, Å (Å$=10^{-10}$ m) or nanometer, nm (1 nm$=10^{-9}$ m).

(*ii*) **Frequency.** It is the number of complete cycles (waves) or wave crests that pass a given point in 1 second. It is usually represented as cycles per second (cps), *i.e.*, second^{-1} which is given the special name *hertz* (Hz).

$$1 \text{ Hz} = 1 \text{ s}^{-1}$$

A frequency of 20 Hz means that 20 wave crests pass a given point in 1 s. It is designated by the Greek letter nu, ν. If there are ν waves per second that pass a given point, and if the length of each wave is λ. The distance travelled by the wave in 1s is $\lambda\nu$. This distance travelled is the velocity (or speed) of wave,

$$v = \lambda\nu$$

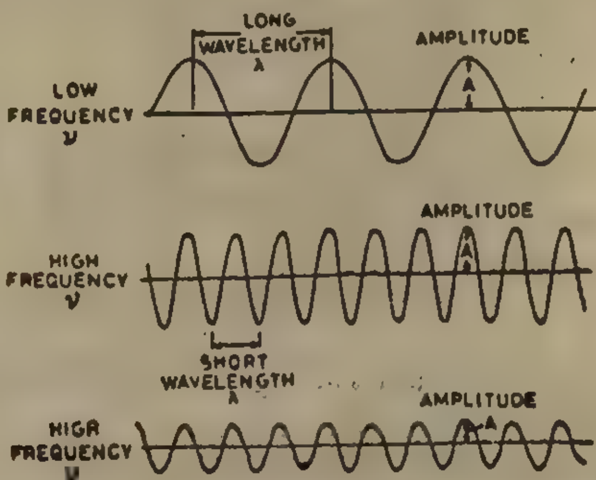

Fig. 1.5. Characteristics of waves. Any wave can be described by its wave length, frequency, amplitude, and speed ($C=\lambda\nu$). The energy of a wave is conveyed by its amplitude.

(*iii*) **Velocity.** Thus the distance travelled by the wave front in one second is called its velocity (v).

Since light and all other types of electromagnetic radiations have a velocity of $3{\cdot}00 \times 10^8$ ms^{-1} in vacuum; this velocity is given the symbol c,

$$c = \lambda\nu = 3{\cdot}00 \times 10^8 \text{ ms}^{-1}$$

(*iv*) **Amplitude.** It is the height of a crest or the depth of a trough. It is designated by the letter, A. The energy per unit volume stored in a wave is proportional to A^2. For light, the intensity or brightness is proportional to A^2.

(*v*) **Wave number.** It is the number of wave crests traversed per unit length. It is designated by $\bar{v}$. It is expressed in units of reciprocal centimetres, 1/cm or cm^{-1}. It is the reciprocal of wavelength, *i.e.*,

$$\bar{v} = \frac{1}{\lambda}.$$

1.4. THE DE BROGLIE RELATION

Louis de Broglie suggested that the electron should, under certain circumstances, show the properties which are associated with wave phenomena. He developed a theory for moving electrons based on the wave and particle behaviour of electrons He suggested that for a particle of mass, m and velocity, v moving freely in space, its wavelength would be given by the expression,

$$\lambda = \frac{h}{mv} = \frac{h}{p} \qquad \ldots(1.1)$$

Where the product $m\,v$ is the momentum (p) of the particle and h is the Planck's constant (utilised by Planck to relate energy to frequency, *i.e.*, $E=hv$). This expression* is an outgrowth of Planck's quantum theory and Einstein's theory of relativity.

This relationship has been fully verified by experiments performed by C. Davisson and L. H. Germer (1927) and George Thomson.

Using the relation of de Broglie, the wavelengths of various particles moving with various speeds can be calculated. The equation

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*Most of the phenomena pertaining to light are described in terms of wave nature. A photon of light behaves both like a particle and a wave. It turned out that photons follow the two fundamental expressions.

$$E = h\nu \quad \text{(Planck's equation)} \qquad \ldots(i)$$
$$E = mc^2 \quad \text{(Einstein's equation)} \qquad \ldots(ii)$$

Combining the two expressions

$$mc^2 = h\nu \text{ or } \frac{h\nu}{c} = mc \qquad \ldots(iii)$$

Since $\lambda = c/\nu$; substituting the value of ν in equation (*iii*)

$$\frac{hc}{\lambda c} = mc \text{ or } \frac{h}{\lambda} = mc \text{ or } \lambda = \frac{h}{mc}.$$

The above expression is called the de Broglie equation and it correlates the particle properties such as mass with wave properties such as wavelength. de Broglie assumed the same relationship for the motion of particles such as electron, *viz.*,

$$\lambda = \frac{h}{m\nu} \text{ where } \nu \text{ is the velocity.}$$

shows that as the velocity or mass or both increase, the wavelength decreases correspondingly. Massive objects have de Broglie wavelengths so short that it is difficult to measure them with accuracy. Consequently, the concept of the duality of matter is of importance only for particles such as electrons

Of course, de Broglie's equation could not be $E=\frac{hc}{\lambda}$ because matter is not electromagnetic radiation. As particles of matter oscillate at various frequencies, radiation can be emitted. Although, "matter waves" possess the typical properties of waves (ν, λ, *etc.*), they cannot move at the speed of light and should not be confused with light. The de Broglie's relation between wavelength and momentum is illustrated in Fig. 1.6.

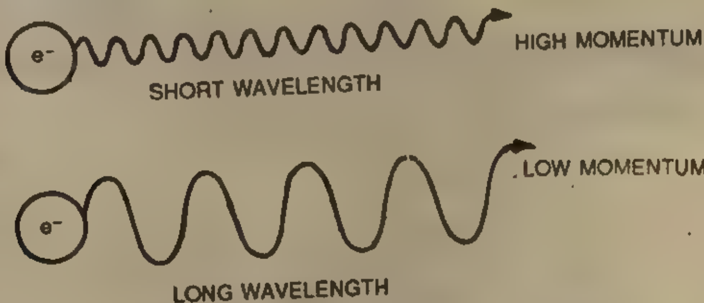

Fig. 1.6. Illustration of the de Broglie hypothesis.

Exercise 1.1. *The mass of an electron is* $9{\cdot}11\times10^{-31}$ kg. *What is the wavelength of an electron with a speed of* $6{\cdot}12\times10^{6}$ m s^{-1} ?

Solution : From the de Broglie equation we have

$$\lambda=\frac{h}{mv}$$

The value of Planck constant, h is $6{\cdot}63\times10^{-34}$ J. In SI units h is $6{\cdot}63\times10^{-34}$ kg m^2 s^{-1}.

(Since the unit conversion factor 1 kg m^2 s^{-}=1 J).

$$\lambda=\frac{h}{mv}$$

$$=\frac{6.63\times10^{-34}\ \text{kg m}^2\text{s}^{-1}}{9.11\times10^{-31}\ \text{kg}\times6.12\times10^{6}\ \text{m s}^{-1}}$$

$$=1.19\times10^{-10}\ \text{m}$$

$$=1.19\times10^{-1}\ \text{nm}$$

$$=0.119\ \text{nm}$$

Thus, the wavelength of electrons moving with a speed $6{\cdot}12\times10^{6}$ m s^{-1} is comparable with the wavelength of *X*-rays.

Exercise 1.2. *The wavelength of a beam of light is 2.8×10^{-5} m. Calculate its (i) wavelength in* cm, *(ii) frequency, and (iii) the energy of one of its photon.*

Solution : (*i*) Wavelength of a beam of light in cm is $2{\cdot}8 \times 10^{-3}$ cm.

(*ii*) By substituting the value of speed of light and that of wavelength in the relation $c = \lambda \nu$, we get

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^{8}\ \mathrm{ms^{-1}}}{2.8 \times 10^{-6}\ \mathrm{m}}$$

$$= 1.07 \times 10^{15}\ \mathrm{s^{-1}}$$

(*ii*) $$E = h\nu$$

$$= 6{\cdot}6 \times 10^{-34}\ \mathrm{J \times s} \times 1.07 \times 10^{13}\ \mathrm{s^{-1}}$$

$$= 7{\cdot}062 \times 10^{-21}\ \mathrm{J}.$$

Exercise 1.3. *Calculate the momentum of a particle which has a de Broglie wavelength of $0{\cdot}1$* nm.

Solution : From the de Broglie expression

$$\lambda = \frac{h}{mv}$$

$$mv = \frac{h}{\lambda}$$

$$= \frac{6{\cdot}6 \times 10^{-34}\ \mathrm{kg\ m^2\ s^{-1}}}{10^{-10}\ \mathrm{m}}$$

$$= 6{\cdot}6 \times 10^{24}\ \mathrm{kg\ m\ s^{-1}}$$

Exercise 1.4. *Calculate the wavelength of an electron moving at 3.0×10^{10}* cm s^{-1} *and of a base ball of 100 g moving at 3.0×10^{3}* cm s^{-1}.

Solution : The mass of an electron is $= 9.1 \times 13^{-31}$ kg ; h is 6.6×10^{-34} Js or kg m^2 s^{-1} ; v is 3×10^{10} cm s^{-1} or 3×10^{8} m s^{-1}. Thus, substituting the value of m, h and v in the relation,

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.6 \times 10^{-34}\ \mathrm{kg\ m^2\ s^{-1}}}{9.1 \times 10^{-31} \times 3 \times 10^{8}\ \mathrm{kg \times m\ s^{-1}}}$$

$$= 2.4 \times 10^{-12}\ \mathrm{m}$$

The mass of a base ball is 100 g or 0.1 kg ; v is 3×10^{3} cm s^{-1} or 3×10 m s^{-1}.

Substituting for m, h and v :

$$= \frac{6.6 \times 10^{-34}\ \mathrm{kg\ m^2\ s^{-1}}}{0.1 \times 3 \times 10\mathrm{kg \times m\ s^{-1}}}$$

$$= 2.2 \times 10^{-34}\ \mathrm{m}$$

Thus, from the wavelengths of an electron and a base ball, it is evident that light particles like electron follow de Broglie equation and massive bodies like a base ball do not follow.

1.5. THE UNCERTAINTY PRINCIPLE

According to the de Broglie relation, the term momentum, p signifies the particle nature of matter and the term wavelength, λ signifies its wave nature. From the relation one can infer that the particle nature is inversely related to wave nature as both p and λ are inversely related to each other. For a massive object, the de Broglie's wavelength is too small to be determined experimentally. Hence, in such cases the wave nature has no significance, but only the corpuscular nature. The motion of such an object is governed by Newton's classical law of motion and can be described by a well defined trajectory. The trajectory of such an object (or particle) can be known by its initial position and velocity at various intervals of time. The exact point of impact of a rocket in action can be determined if we know its position at a particular instant and its velocity at that instant. Thus, the initial position of the rocket, its velocity at various intervals of time and certain other variables determine its trajectory with a desired degree of accuracy.

However, the same is not true for a subatomic particle such as the electron, which besides having particle nature also has significant wave nature. Is it possible to define the position of an electron in space ? If it behaves like a particle, we should be able to locate it precisely. But if it behaves like wave, we cannot do so.

A German physicist, Werner Heisenberg, tried in various ways to ascertain the position of an orbiting electron but all in vain. In 1927, he concluded that there are definite limitations on the accuracy with which one can define the position of an electron.

According to him, **it is not possible to think of a device with the help of which one can determine simultaneously the position and momentum of subatomic particles in motion accurately.**

According to this principle, the more accurately one of these variables is specified, the more uncertain is the other. For instance, if velocity (or momentum) of a particle is determined with great accuracy, its position becomes correspondingly less precise. Similarly, if the position is determined precisely, the momentum of the particle is not known with certainty. Heisenberg showed that the lower limit of this uncertainty is Planck's constant divided by 4π.

Thus,

$$\Delta p_x \Delta x \geqslant \frac{h}{4\pi} \qquad ...(1.2)$$

Here Δp_x is the uncertainty in the momentum in the X direction and Δx is the uncertainty in the position. The sign $\geqslant$

means that the term Δp_x, Δx can be either greater than or equal to but never smaller than $h/4\pi$. If Δp_x is decreased, Δx increases and vice versa.

One of the direct consequences of the uncertainty principle is that the subatomic particles such as electrons cannot have well-defined trajectories, since for such particles both the position and velocity cannot have precise values.

To understand this principle, suppose that we wish to determine the position of an electron at an exact place in space relative to the nucleus of an atom. To achieve this, we must be able to see the electron. To see (to locate) the electron with a desired accuracy we have to use light of appropriately small wavelength. However, light too has a dual nature. From a particle point of view observing an electron requires the interaction of light (photon) with the electron. Light photons of a certain wavelength have a momentum given by $p=mv=h/\lambda$. An unknown part of this momentum is transferred to the electron in the interacting collision (light with small wavelength helps in locating the electron). As a consequence, this alters the velocity of the electron by an unknown amount and its position as well. If we reduce the collision effect by decreasing the momentum of the photon, we find that for photons of sufficiently low momentum, it is no longer possible to locate the electron.* This point has been illustrated in Fig. 1.6.

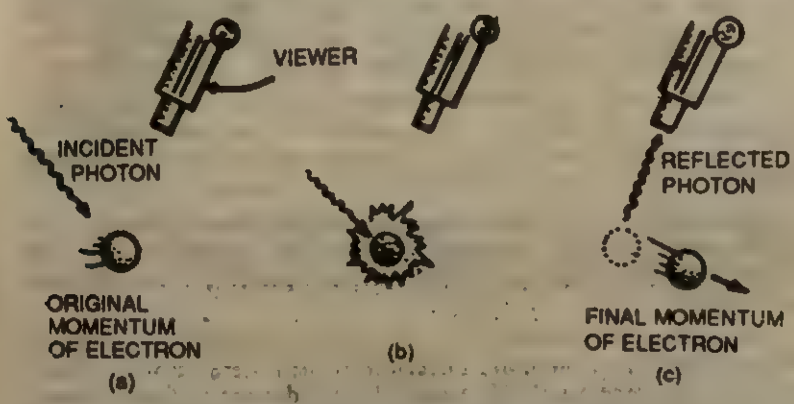

Fig. 1.7. *An electron under investigation* : (*a*) *can only be seen by reflected light* ; (*b*) *incident photon strikes the electron, however, momentum is transferred to the electron and it moves out of focus* ; (*c*) *thus, the exact position cannot be determined.*

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*By decreasing the momentum of photon the value of λ will become large (de Broglie equation). Thus, it leads to the determination of position with great uncertainty. Therefore, in principle, it is possible to assess the position of an object with great accuracy only at the sacrifice of information regarding its momentum and *vice versa*.

For large objects the uncertainties are insignificant. The light falling on a base ball does not disturb it much and uncertainties in position and momentum are far too small to be measured. However, for particles like electrons, this is not true.

Exercise 1.5. *What is the product of uncertainty in position and velocity for an electron of mass 9.11×10^{-28} g according to Heisenberg's uncertainty principle ?*

Solution : From Heisenberg's uncertainty principle,

$$\Delta x \,.\, \Delta p_x = \frac{h}{4\pi} \text{ or } \Delta x \, m \, \Delta v = \frac{h}{4\pi}$$

$$\Delta x \,.\, \Delta v = \frac{h}{m \, 4\pi}$$

Substituting the value of m of an electron, we obtain

$$\Delta x \,.\, \Delta v = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 22 \times \frac{9.1}{7} \times 10^{-31} \text{ kg}}$$

$$= 57 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$$

1.6. THE QUANTUM MECHANICAL MODEL OF THE ATOM

The laws of classical physics (Newtonian mechanics) were, at one time, thought of as universal truths. These laws could only account for large bodies in motion. However, they have failed to describe the motion of subatomic particles properly in the context of the wave-particle duality and the uncertainty principle.

In the Bohr's model, the electron is treated as a particle. According to the model, it is possible to determine both the radius of an orbit and the velocity of an electron in this orbit. The orbit accounts for the precise position of an electron and the velocity for electron momentum. This model violates the de Broglie proposal and the uncertainty principle. This model was replaced by the present quantum mechanical model. Subatomic particles could be described much better by **quantum mechanics (wave mechanics)**, because the main idea of this kind of mechanics is the quantization of energy. The model speaks of the wave-particle duality and the probability of finding an electron within specified regions in space. On the basis of these ideas in mind, we can now list the postulates of quantum mechanics :

1. Electrons in atoms can exist in certain energy states that are characterized by definite energies. When an electron changes its energy state, it must absorb or emit just enough energy to bring it to the new energy state (the quantum condition).
2. When electrons absorb or emit radiations as they change their energies, the frequency of the light is related to the energy change by a simple equation

$$\Delta E = h\nu \qquad (1.3)$$

or $$\Delta E = \frac{hc}{\lambda} \qquad \left(\text{Since} \quad \nu = \frac{c}{\lambda}\right) \qquad ...(1.4)$$

The equation (1.4) gives a relationship between the energy change ($\triangle E$) and the wavelength (λ) of radiation absorbed or emitted. The energy gained (or lost) by an electron as it goes from lower to higher (or higher to lower) energy states is equal to the energy of the photon absorbed (or emitted) during the transition.

3. The allowed energy states can be described by sets of numbers called **quantum numbers**.

In 1926, E. Schrödinger proposed the wave theory to explain the behaviour of the electron in the hydrogen atom. The treatment is highly mathematical because it involves the equations (represented by the symbol ψ) of the electron as a wave. The mathematical equation to represent the behaviour of electron is

$$\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+\frac{8\pi^2 m_e}{h^2}(E-V)\,\psi=0 \qquad ...(1.5)$$

Where E is the total energy ; m, e and V are the mass, charge and the potential energy of the electron in the atom respectively. The variable ψ (psi) is a time-independent amplitude function though it is commonly called simply the '**wave function**'. The mathematical equation, ψ is a function of three coordinates (such as x, y and z or r, θ and ϕ) which are used to designate the electron within the atom with nucleus as the origin. A wave equation is not much like an algebraic equation. It is of a type known as a differential equation which has series of solutions. These solutions can be obtained only under certain conditions. If the electron is to be treated a wave, then an integral number of wavelengths must be fitted into one circuit of the electron. (Fig. 1.8).

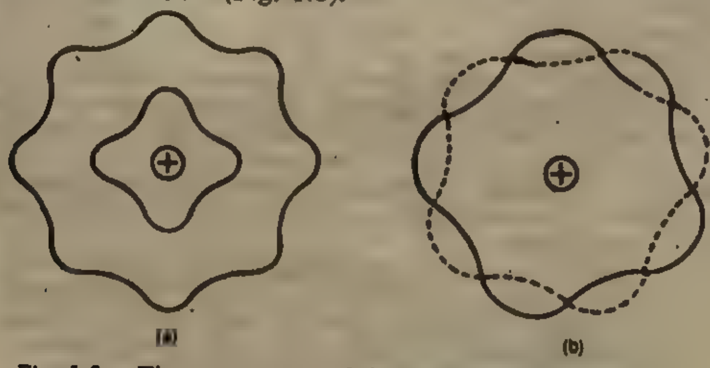


Fig. 1.8. The wave nature of the electron : (a) Integral number of wavelengths. Crests and troughs of the waves match exactly for consecutive circuits about the nucleus. (b) The number of wavelengths is not integral and destructive interference occurs. Crest in one circuit is cancelled by a trough on the next.

As we know solutions to a differential equation (1.5) are numerous, but for a standing wave only certain solutions are permissible. The equation may be solved by transforming to a system of spherical polar co-ordinates in place of the cartesian co-ordinates system of x, y and z. The wave equation then becomes a function of three variables, r (radial), and θ and ϕ (angular); this conversion allows the equation to be broken down into three similar equations that depend on r, θ and ϕ separately. Solutions to these equations also depend upon certain constants which, in turn, can be shown to be integral numbers and have been identified as **quantum numbers**, n, l and m_l since they represent the quantization of definite physical properties about the electron in the atom.

For the hydrogen atom, in the ground state, several solutions, (*i.e.*, wave functions) are obtained. Each wave function describes a possible state (or orbital) of the electron in the atom. The wave function, ψ, itself has no physical interpretation which can be positive or negative, the square of its absolute magnitude, ψ^2 evaluated at a particular place for a given set of co-ordinates at a particular time is proportional to the probability of finding the electron at that time. The momentum, angular momentum and the energy of the electron can be established from ψ. The problem of representing ψ^2 is considered in two parts, one a radial part and the other an angular part.

As understood, the solution of the wave equation gives a set of numbers, called quantum numbers, that describe the energies of electrons in atoms. Solutions also give information about the shapes and orientations of the statistically most probable distributions of the electrons around the nucleus. Wave functions describing single electrons are called **orbital wave functions or simply orbitals.** The name is intended to be similar to the term orbit used in Bohr theory but also to be different.

For an electron in an orbital does not mean moving along a Bohr's path or trajectory. Instead, it gives a probability description of where the electron is likely to be found. These orbitals are directly related to the quantum numbers. We must, therefore, now describe the quantum numbers.

1.7. ORBITALS AND QUANTUM NUMBERS

According to wave mechanics, the energy levels in the atom are composed of one or more orbitals. In atoms that have more than one electron, the distribution of the electrons about the nucleus is described by the number and type of energy levels that are occupied. Therefore, to understand the arrangement of electrons in space it is necessary to examine the energy levels. This is best accomplished through a discussion of quantum numbers. These quantum numbers are needed to describe an electron orbital in three dimensions.

The first and perhaps the most important quantum number is called the **principal quantum number** which is symbolized by letter '*n*'. It refers to the average distance of an electron from the nucleus. The distance is related to the energy of the electron. '*n*' can have positive integral values 1, 2, 3 and so on ....upto ∞ referring to the first (or K), second (or L), third (or M), *etc.*, main energy levels of the electrons in an atom.

The principal quantum number, *n*, in combination with another quantum number, *l* (to be discussed later) describes the radial distribution of an electron. The term radial distribution conveys about the probability distribution of the electron as a function of its distance from the nucleus.

Since the energy of the electron depends upon its distance from the nucleus, it is obvious that *n* also conveys about the size of the orbital. The term size depicts the effective volume of an orbital in which there is 90 to 95% probability of finding the electron. The maximum probability of finding an electron is at a distance 0·053 nm. The size of the orbital increases as the value of the *n* is increased.

The second quantum number is known as **angular momentum quantum number** as it denotes the angular momentum. It is also known as **azimuthal, orbital, subsidiary or secondary quantum number**. It is designated by the letter *l*. It determines the shape of the spatial region in which the electron is most probably found (Fig 1.9). It turns out that the numerical values for '*l*' can again be only integral number 0, 1, 2, 3...... upto $n-1$, *i.e.*, it can have more than one value depending upon the value of *n* (Table 1.1).

TABLE 1·1. Permissible values of *l* for a given value of *n*.

Value of n	*Permissible values of l*
1	0
2	0 and 1
3	0, 1 and 2
4	0, 1, 1 2 and 3
... and so on	0, 1, ...($n-1$)

The value of *l* is also symbolized by the symbols (Table 1.2) reserved for the shape of the orbital.

TABLE 1.2 Designation of quantum number *l* by the symbols

Value of l	*Designation*	*Probable shape*
0	s	Spherical
1	p	Dumb-bell
2	d	Double dumb-bell
3	f	Difficult to depict (complex)
4	g	......
...... and so on	......	......

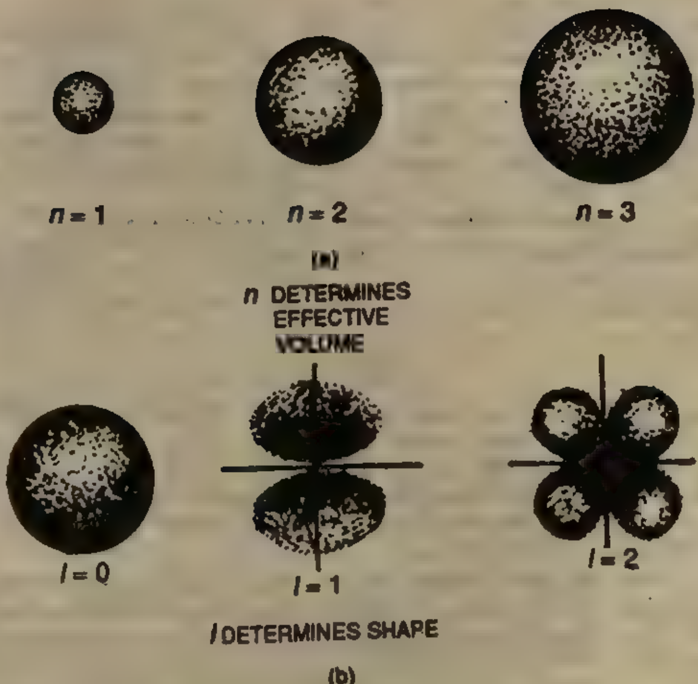


Fig. 1.9. Spatial representation of the region of electron motion defined by n and l quantum numbers.

Thus for each value of *l*, a letter has become associated, each corresponding to a different kind of atomic orbital. The s, p, d and f designations arise from the characteristics of spectral emission lines produced by electrons occupying the orbitals ; s (sharp), p (principal), d (diffuse), f (fine structure, ...) An orbital in an atom is designated by denoting the values of both the quantum numbers *n* and *l*.

The third magnetic quantum number designates the spatial orientation of an atomic orbital It has the symbol m_l because it controls the behaviour of *l* in a magnetic field.

The magnetic quantum number determines the direction of angular momentum. The magnitude of angular momentum is determined by the azimuthal quantum number, *l*. Thus, the magnetic quantum number, m_l conveys about the space quantization of angular momentum. When an atom is placed in a magnetic field, the angular momentum of the electron assumes only some specific orientations with respect to the any particular axis (say *z*-axis ; the *z*-component is conventionally fixed by the direction of the magnetic field) such that the components of this vector (angular momentum)

must also be integral, *i.e.*, it should have quantized values. These orientations can be such that l has components pointing with the field or against it, so that there are equal number of positive and nagative values of m_l. These values range from $\pm l$ to zero in integral steps From examination of the allowed values of m_l for a given value of l, it can be seen that there are $(2l+1)$ ways of assigning m_l (l positive values, l negative values and zero), *i.e.*, $m_l=0, \pm 1, \pm 2 \cdots\cdots \pm l$ These are described in Table 1.3.

Table 1.3 Permissible values of m_l for a specified value of l

Azimuthal quantum number, l	*Permissible values of m_l*	*Number of values (2l+1)*
0	0	1
1	+1, 0, −1	3
2	+2, +1, 0, −1, −2	5
3	+3, +2, +1, 0, −1, −2, −3	7
..........and so on	...+l ...0 ...−l,	2l+1

Clearly, the total permissible values of m_l for a designated value of l gives the number of orbitals of one type within a sub-shell (or orbital). For example, for $l=0$ there is one orbital of s type, for $l=1$ there are three p-orbitals and five d-orbitals (d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{yz} and d_{xz}) if $l=2$ and so on.

Since the quantum number, m_l dictates the direction of angular momentum, this number also dictates the direction of the orbital in space. For example, there are three orbitals of p-type ($l=1$) corresponding to the three values of m_l (*i e.*, +1, 0, −1). The plots of p_0, $p_{+1}+p_{-1}$, and $p_{+1}-p_{-1}$ assume dumb-bell shape and are mutually perpendicular to one another pointing towards z, x and y-axis respectively. Because of their orientation, they are also designated as p_z, p_x and p_y orbitals respectively (Fig. 1.10).

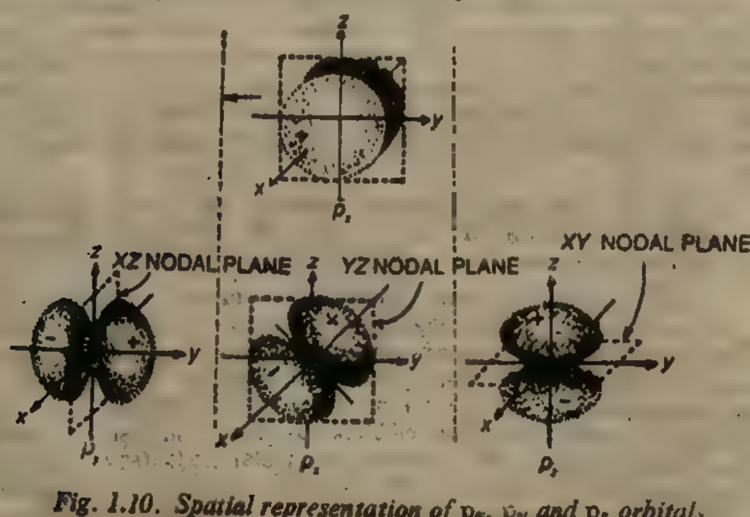


Fig. 1.10. Spatial representation of p_x, p_y and p_z orbitals.

There is one orbital of s-type when $l=0$. Its plot assumes spherical shape around the nucleus and hence no direction. The electron density is symmetrically distributed in all directions.

The **spin quantum number**, m_s refers to the spin of an electron around its own axis and the orientation of the magnetic field produced by the spin of that electron. Thus the spinning electron produces angular momentum whose z-component (by convention) is also quantized in half-integer units. For every set of n, l and m_l values, m_s can take the value of $+\frac{1}{2}$ or $-\frac{1}{2}$. The spinning of the electron with $m_s=+\frac{1}{2}$ is conventionally known as α-spin and is represented by a vertical arrow ($\uparrow$). The spinning of the electron with $m_s=-\frac{1}{2}$ is known as β-spin and is shown by a downward arrow ($\downarrow$).

Hence, an electron in an orbital has a characteristic set of four quantum numbers.

Energies of atomic orbitals

Every permitted combination of the three quantum numbers, n, l and m_l (a set of permitted values for the orbital) corresponds to a different electron orbital. All orbitals with same value of the principal quantum number, n are said to be in the same principal electronic shell or principal level and all orbitals with same value of l are in the same subshell or sublevel.

The principal shells are numbered according to the value of n.

In a one electron system (such as H, He^+ and Li^{2+}), the energy of the electron is determined by the value of the principal quantum number only with the help of expression

$$E_n = -\frac{1}{n^2}\left(\frac{2\pi^2 mz^2e^4}{h^2}\right) \qquad ...(1.6)$$

in which m=mass of the electron, e=the value of the charge on the electron, z=number of charges, h=Planck constant, n=an integer of values 1, 2, 3,......, and E_n=energy of state n. Since Bohr used quantum theory to propose the existence of allowed states, they are known as quantum states of the atom. The integer 'n' which determines the energy is called a quantum number.

The energy (E_n) of each stationary state in the hydrogen atom is,

$$E_n = -\frac{1312}{n^2} \text{ kJ mol}^{-1} \qquad ...(1.7)$$

The lowest permissible value of the lowest energy level, called the ground state has a value of -1312 kJ mol^{-1}. The negative sign is used to provide agreement with the convention that potential energy of attraction has a negative value. The negative sign depicts that the electron is bound to the nucleus, hence, it is in a more stable state than one in which the proton and electron are separated by an infinite distance. In other words, the electron in hydrogn atom has less energy, *i.e.*, the atom is more stable. The potential energy is zero when the electron is far removed from the nucleus, *i.e* , when the hydrogen atom is ionized. Thus, to ionize a hydrogen atom a minimum of 1312 *k*J mol^{-1} of energy is required for hydrogen atoms.

The ionization energy of an isolated gaseous hydrogen atom is, therefore, 1312 kJ.

Thus, the values of E represent the permitted values for the energy of the nydrogen atom. The hydrogen atom cannot exist with an energy other than those permitted by equation (1.6). These allowed states are described by the integral values of n. Accordingly, the first permitted energy state is E_1 $(n=1)$, the second permitted energy state is E_2 $(n=2)$, and so on.

If we designate $\dfrac{2\pi mz^2e^4}{h^2}$ by E_0, we observe that.

$$E_1=-\frac{E_0}{1^2}=-E_0=-1312 \text{ kJ mol}^{-1}$$

$$E_2=-\frac{E_0}{2^2}=-\frac{E_0}{4}=-328 \text{ kJ mol}^{-1}$$

$$E_3=-\frac{E_0}{3^2}=-\frac{E_0}{9}=-146 \text{ kJ mol}^{-1}$$

$$E_4=-\frac{E_0}{4^2}=-\frac{E_0}{16}=-82 \text{ kJ mol}^{-1}$$

For a given value of n, the total permitted values of l are n and these designate various subshells (orbitals) within the principal quantum shell. For one electron (hydrogen like) system, the various subshells are degenerate in energy, *i.e.*, they all have the same energy. For a system with more than one electron, the energies of various subshells in a principal shell increase with the increase in the value of quantum number l. Thus the energy increases with the increase in the value of $n+l$ within a specific quantum shell.

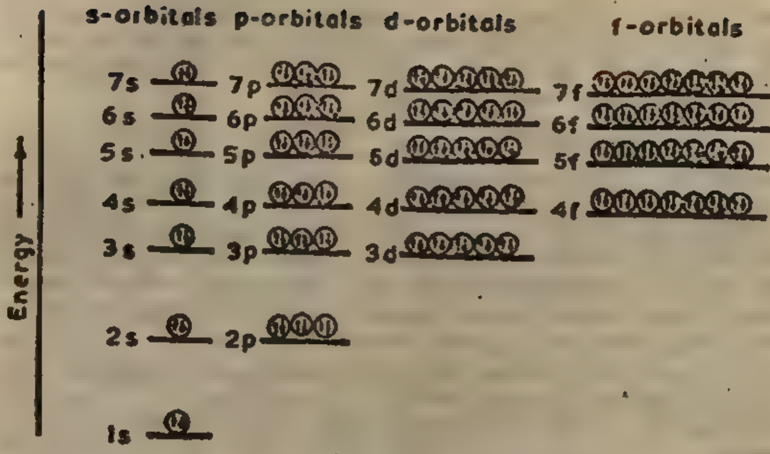


Fig. 1.11. Energy level diagram for hydrogen. The circles depict orbitals. The various orbitals have different energies and are arranged in the increasing order of energy. In the case of hydrogen, energy levels are a function of principal quantum number. Hence, all the orbitals of the given principal shell of the hydrogen atom have the same energy. Orbitals with the same energies are said to be degenerate.

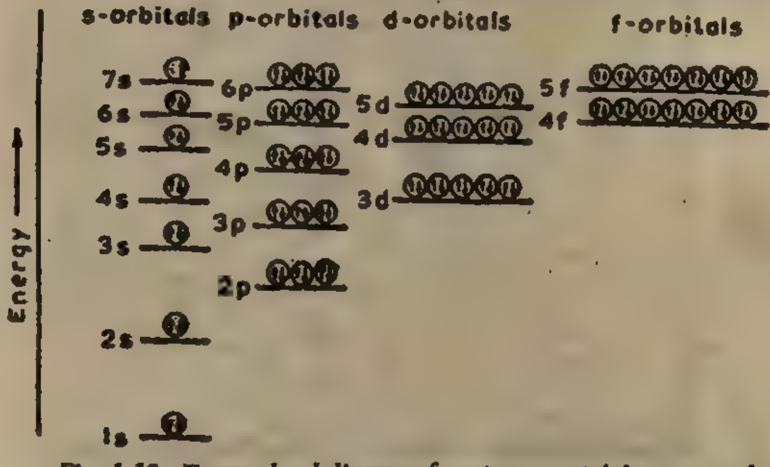


Fig. 1.12. Energy level diagram for atoms containing more than one electron.

1.8. SHAPES OF ORBITALS

Each solution (called a wave function, ψ), of wave equation corresponds to a different energy state. Thus, in quantum mechanics it is not necessary to assume quantization of energy as it has been in the

case of Bohr's atomic model. It happens as a direct consequence of the electron's wave-like behaviour. The first solution in the terms of ψ and r and the angular direction to the wave equation for the hydrogen atom can be written as,

$$\psi_{1s}=Ae^{-Br} \quad ...(1.8)$$

where A and B are constants, e is the base of natural logarithm and r represents the distance from the nucleus. The value of the wave function, ψ for an electron in an atom is dependent both on the radial distance, r of the electron from the nucleus of the atom and on its angular direction away from the nucleus The dependence of ψ on angular direction introduces the use of polar coordinates (r, θ and ϕ) along with cartesian coordinates.

According to the laws of quantum mechanics, a wave function, ψ has by itself no physical meaning. The square. ψ^2 of the wave function is a measure of the probable electron density at a given point.

In the equation (1.8), the exponent is $-Br$, and because of the

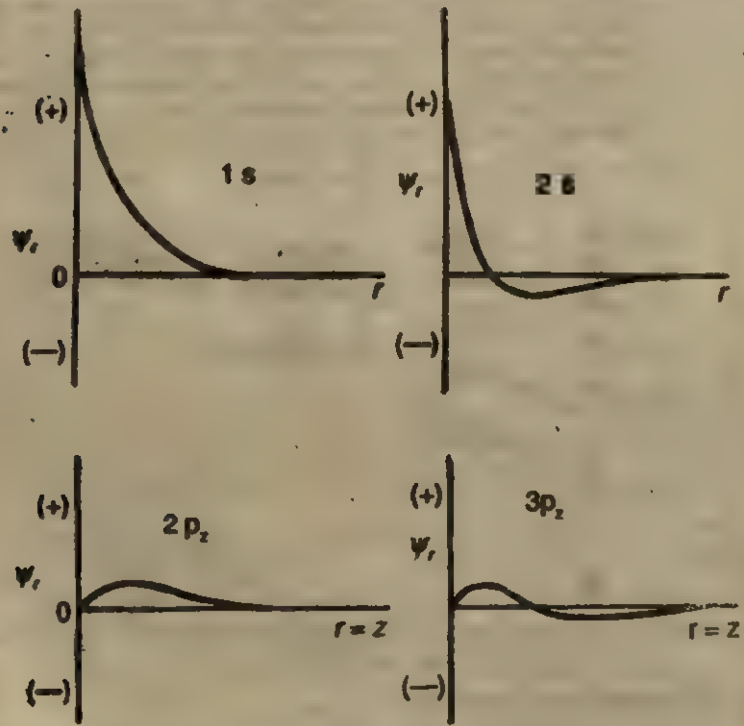


Fig. 1.13. Variation of the magnitude of ψ_r with r for various orbitals

negative sign, ψ will decrease as r increases. This means that the farther we go from the nucleus, the smaller will be the probability of finding the electron. The value of the wave function, $\psi(r)$ as a function of the radial distance from the centre of the atom, r is shown in Fig. 1.13 for 1s, 2s, 2p,...... electron orbitals. These graphs allow us to visualise how the magnitude of the 'electron matter wave' varies with distance from the nucleus. These do not give any direct information regarding electron cloud shapes. For orbitals other than s orbitals, although the shape of $\psi(r)$ does not change with directions, the magnitude of $\psi(r)$ is a maximum for some definite directions and even zero at some distance.

The probable electron density, $\psi^2(r)$ associated with an electron orbital as a function of r is given in Fig. 1.14. For s orbitals, the probability of finding an electron at the nucleus is finite (non-zero), whereas for all other orbitals, the value of $\psi^2(r)$ at the nucleus is zero.

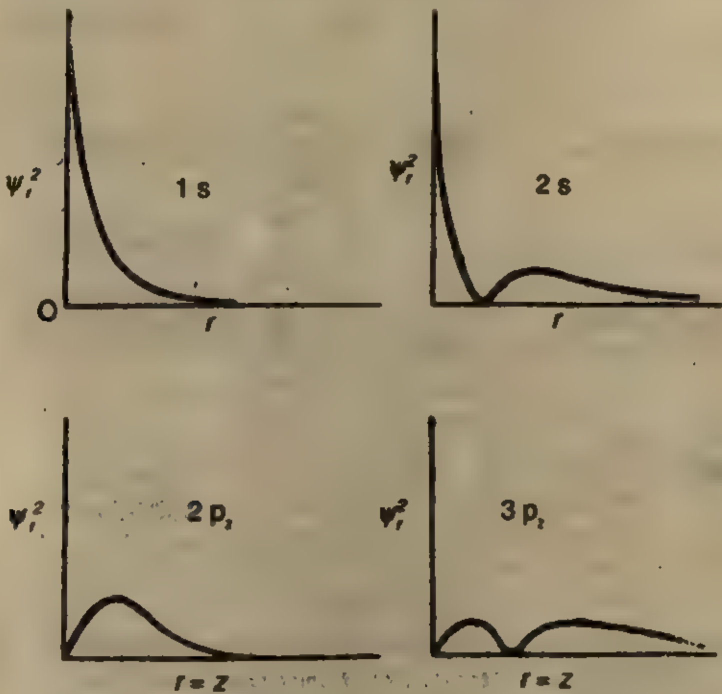


Fig. 1.14. Probability of finding an electron at a point at distance r from the nucleus

Thus, it appears that for s orbitals, the probability is the highest at the point next to the nucleus. It amounts to saying that the electron spends more time near the nucleus and less and less time at distances farther and farther away. In this way, the negative charge of the electron smears out into a cloud (spherical for s orbitals). The density of electronic charge is maximum in the regions where the orbital cloud is thickest; which falls off quite rapidly in moving away from the nucleus in any direction. A pictorial interpretation of the graphs of $\psi^2(r)$ versus r is given in Fig. 1.15(I). In another way of depicting the probability density distribution, a surface boundary is drawn. The surfaces on which every point has the same value of ψ^2 are called boundary surfaces and they enclose 90-95 per cent of the electronic charge. Diagrams of boundary surfaces are much in use because of their easy drawing. Electron clouds, contours of constant probability and boundary surfaces for both 2p and 3p are also illustrated in Fig. 1.15(II).

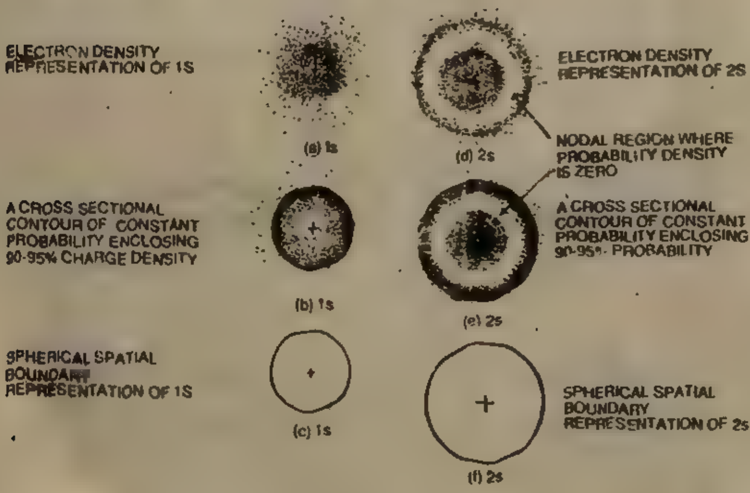


Fig. 1.15. (I) Various representations of the atomic orbitals (1s, 2s); (a, d) variation of the density of the charge cloud of 1s, 2s, orbitals; (b, e) a cross-sectional contour of electronic charge cloud; (c, f) spherical spatial boundary representation enclosing the 90-95 per cent probability region.

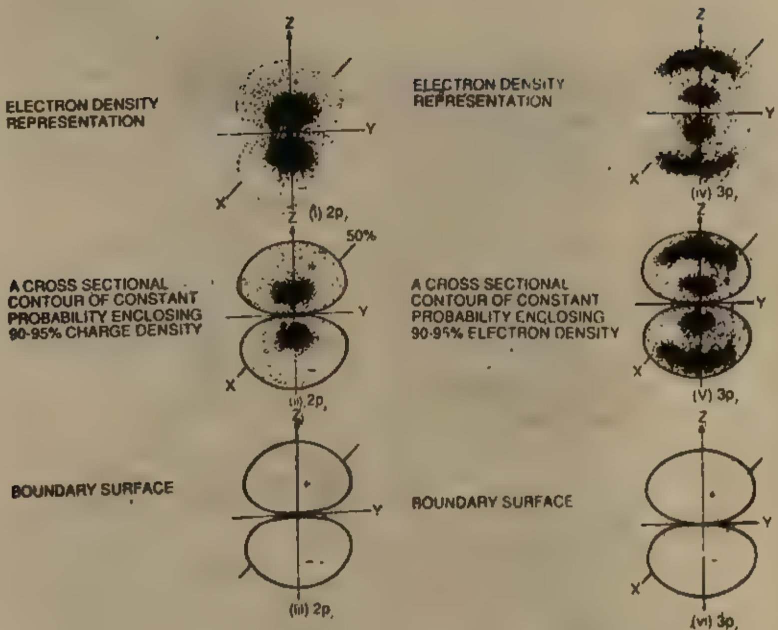


Fig. 1.15. (II) Various representations of the atomic orbitals (2p, 3p) : (i) and (iv) variation of the density of the charge cloud of 2p and 3p orbitals, (ii) and (v) a cross-sectional contour of electron charge cloud, and (iii) and (vi) spatial boundary representation enclosing the 90-95 per cent probability region.

s orbitals. Each s orbital is spherically symmetrical. There is an s orbital for each permissible value of n, denoted as 1s, 2s, 3s and so on. As n increases, the size of the spherical orbital gets larger. The orbital has no preferred direction. The probability of finding an electron at a distance r from the nucleus is the same in all directions. For 2s, 3s,......orbitals, the electron density fluctuates with the distance from the nucleus (Fig. 1.16). In 2s orbital, near the nucleus there is spherical region of high electron density surrounded by a spherical **nodal surface** on which the electron is never found, *i.e.*, for which the probability density ψ^2 is zero.

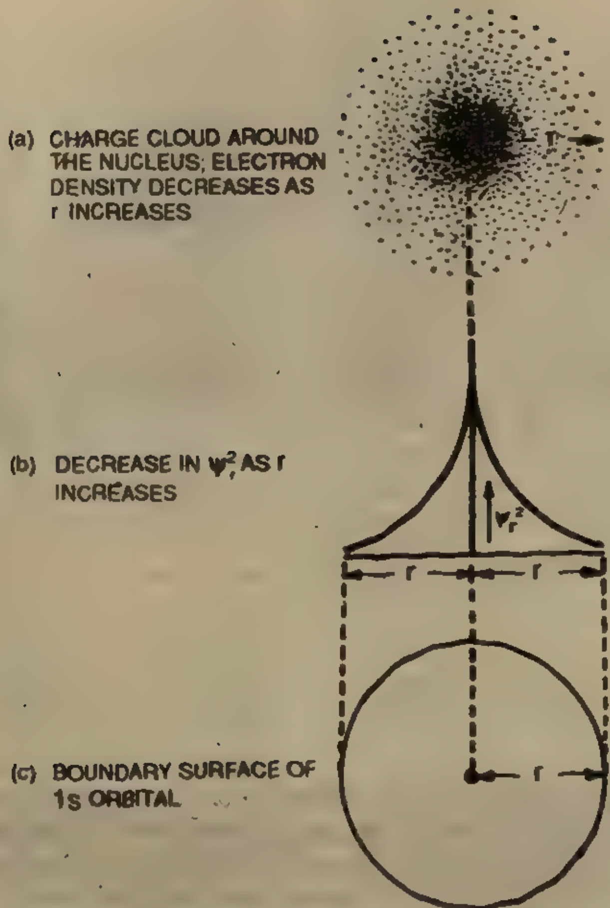


Fig. 1.16. (I) Probability distribution for a 1s atomic orbital based on ψ^2_r values

p orbitals. The set of three 2p orbitals is pictured in Fig. 1.10. The boundary surfaces of these orbitals are identical in shape, but their orientations differ. Each has its electron density concentrated in two lobes (one on either side of the two nucleus ; the plus and minus signs in the two lobes indicate algebraic signs of the wave function, ψ itself) lying on a single axis. The $2p_x$ orbital has the x-axis running through it, and *yz* plane is a node. The *y* and *z* axes

run through $2p_y$ and $2p_z$ orbitals respectively, and their respective nodes are the xz and xy planes.

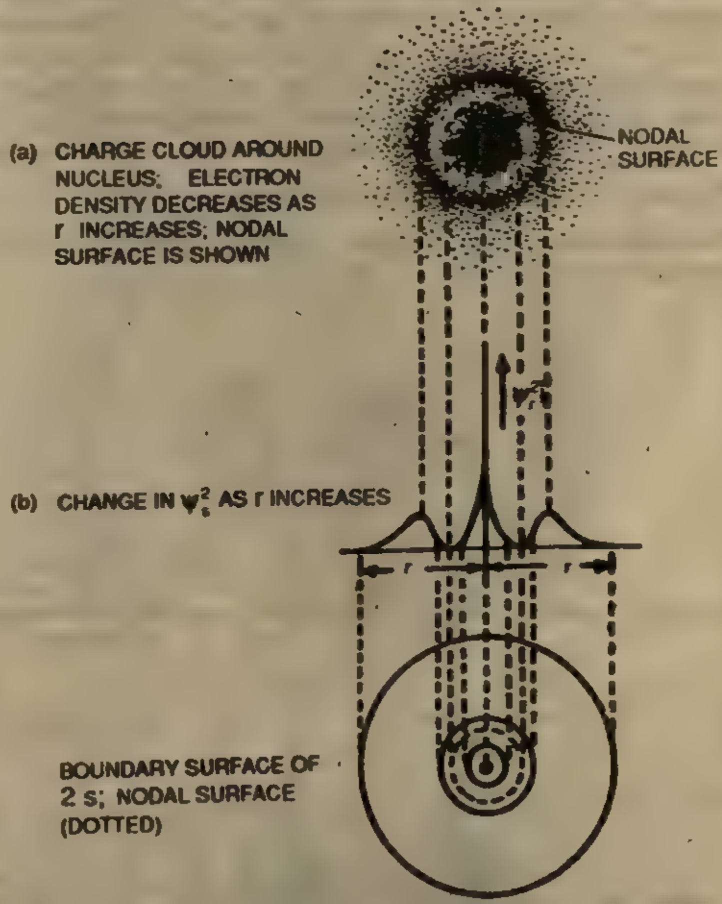


Fig 1.16. (II) Probability distribution for a 2s atomic orbital based on ψ^2_s values.

The probability density curve (Fig. 1.17) for a 2p electron shows the variation in the values of ψ^2 along that axis which runs through lobes. The figure also includes the electronic charge cloud of a 3p electron. A 3p orbital is like a 2p orbital, except that it has one extra radial node. The charge distribution is shown in Fig. 1.17 in which both the probability density plot and the charge cloud are shown.

d orbitals. For $n=3$ nine different orbitals are possible, one 3s orbital, three 3p orbitals and five 3d orbitals. The five 3d orbitals are equivalent in energy and are portrayed in charge cloud representations in Fig. 1.18. The $3d_{xy}$ orbital consists of four lobes, each of which is located between the x and y coordinate axes. The $3d_{yz}$ and $3d_{xz}$ are also similar in shapes but differ in plane that contains the axes. The $3d_{x^2-y^2}$ orbital also has four lobes, but these are oriented so that x and y axes pass through the lobe centres. The $3d_{z^2}$ is different, it has a pair of lobes pointing along the z axis together with a tyre surrounding the z-axis.

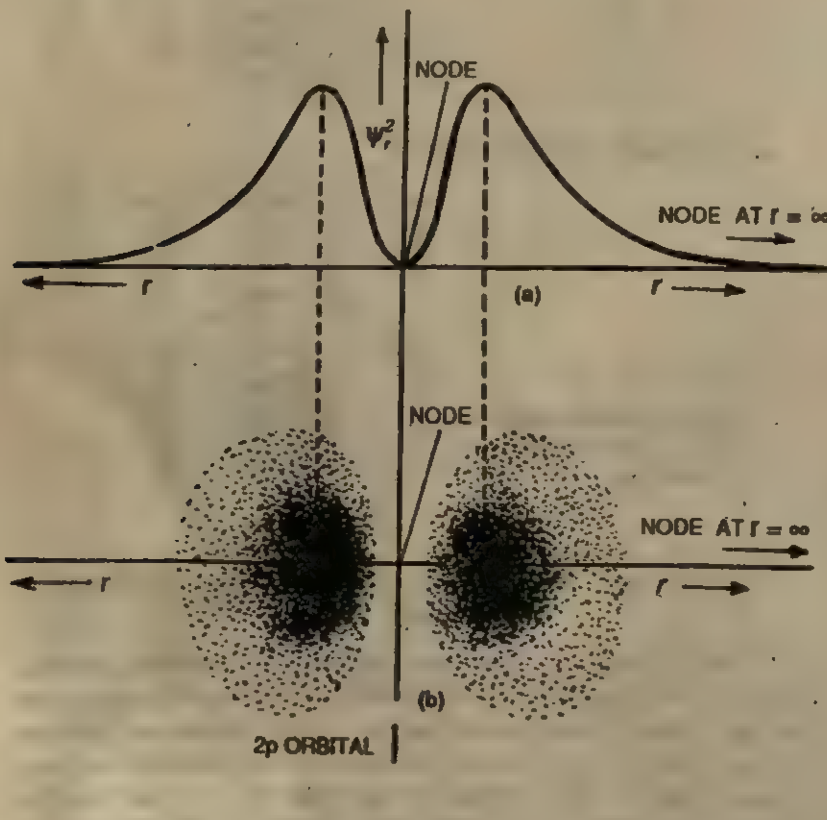


Fig. 1.17. (I) A 2p orbital : (a) Probability-density plot based upon ψ^2_r values. (b) Cross-section of electronic charge cloud.

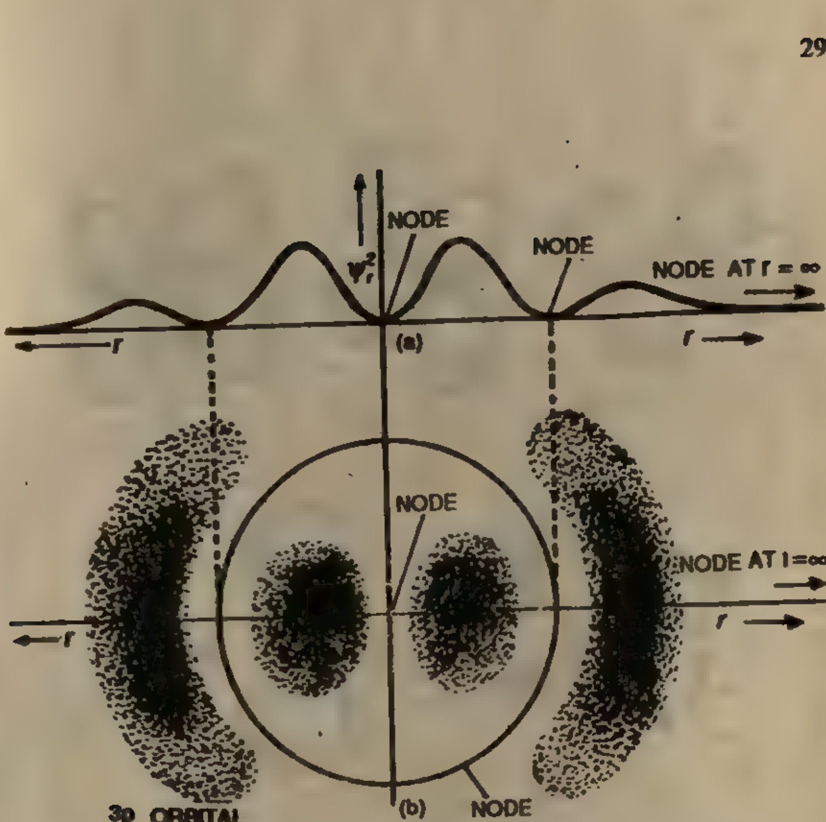


Fig. 1.17 (II) A 3p orbital : (a) Probability-density plot based upon ψ_r^2 values. (b) Cross-section of electronic charge cloud.

1.9. ELECTRON CONFIGURATION OF ATOMS (AUFBAU PRINCIPLE)

A designation which characterizes each electron in an atom is referred to as the electron configuration. The electron configuration of an element depicts the location and energy of the electrons. You are already familiar with the rules of writing the electron configuration of atoms. After learning about orbitals, it becomes appropriate to reconsider the topic and understand some additional features.

An atom in its lowest energy state is said to be in the ground state, stable state or normal state. When an atom contains several electrons, they are assigned to orbitals according to the following

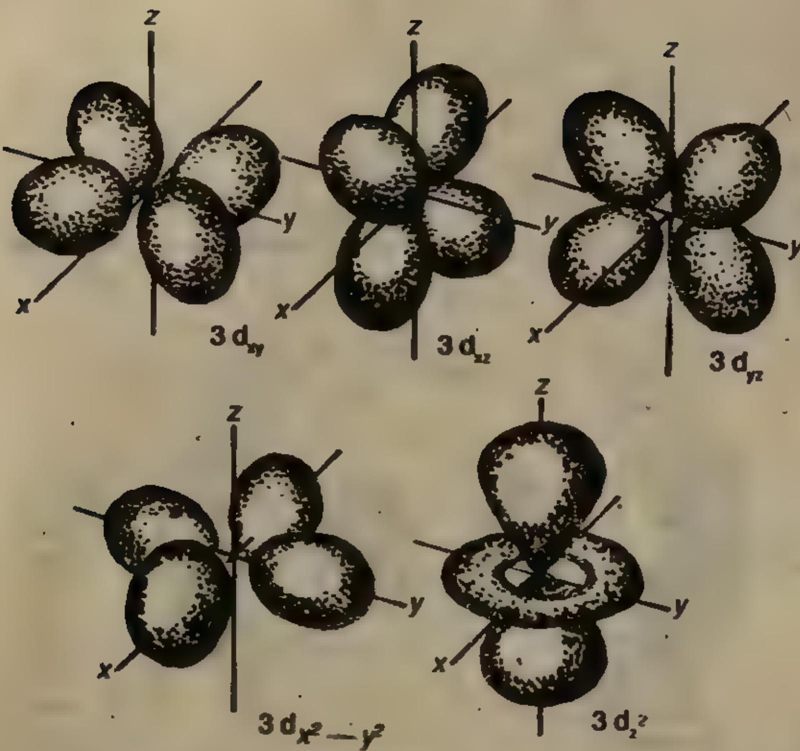


Fig. 1.18. Spatial orientation of d *orbitals. The lobes of* d_{z^2} *and those of* $d_{x^2-y^2}$ *lie along the axes, whereas the lobes of* d_{xy}, d_{yz} *and* d_{zx} *lie along diagonals.*

rules, which are known collectively as the **'Aufbau principle'** (aufbau is a Greek word which means building up).

(*i*) In building up atomic structure, electrons seek to enter the orbital of the lowest energy. For a multi-electron atom, the order is

$$E_{1s} < E_{2s} < E_{2p} < E_{3s} < E_{3p} < E_{4s} < E_{3d} < E_{4p} < E_{5s} < E_{4d} < E_{5p} < E_{6s} < E_{4f} < E_{5d} < E_{6p} \ldots\ldots$$

Several memory devices have been developed to assist in recreating this order of energy levels. The two most common are (Fig. 1.19) :

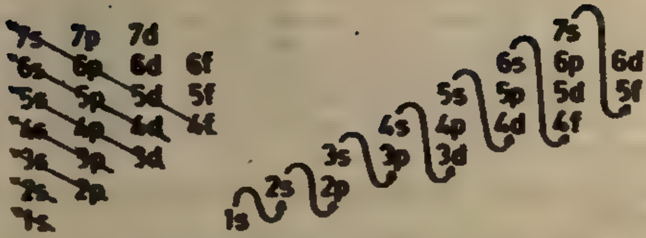
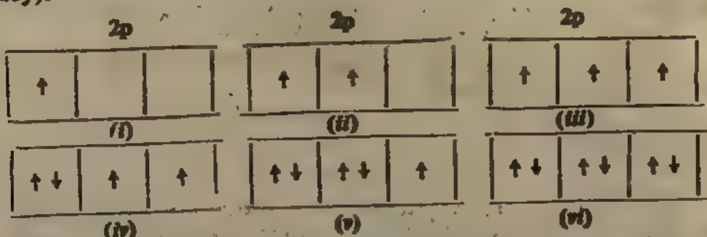


Fig. 1.19. Sequence for filling orbitals. These diagrams are helpful for remembering the order in which the orbitals are filled.

(*ii*) A single orbital cannot have more than two electrons. When two electrons occupy the same orbital they must be of opposite spins (**Pauli's exclusion principle**). Thus two electrons can have the same values for three quantum numbers, n, l and m_l but the fourth quantum number, m_s must have different values of $+\frac{1}{2}$ and $-\frac{1}{2}$ for the two electrons to meet the requirement of the Pauli's exclusion principle. Since within a sub-shell, $2l+1$ orbitals are possible, the maximum number of electrons that can be accommodated are $2(2l+1)$, *i.e.*, 2, 6, 10 and 14 in orbitals s ($l=0$), p ($l=1$), d ($l=2$) and f ($l=3$) respectively.

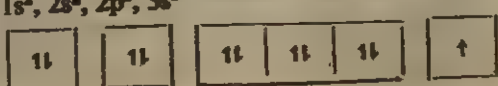
(*iii*) In a set of degenerate orbitals (orbitals of the same energy), electrons with the same spin occupy each orbital singly before any pairing begins (**Hunds rule of maximum multiplicity**).



The filling of 2p orbitals depict the Hund's rule. During the single occupation, the electrons have the same spin either α or β. During the pairing, electrons allign with opposite as required by Pauli's principle to impart stability.

Keeping in view the above given rules, two methods are adopted to designate electron configurations. For example sodium is represented

I. Sodium (Z=11) $1s^2, 2s^2, 2p^6, 3s^1$

II. Sodium (Z=11) 

Method I depicts the total number of electrons in each orbital. Method II gives the break up of each orbital with the help of arrows (orientation of electron spin), upward arrow (↑↓) corresponds to $m_s = +1/2$, (clockwise) and downward (↑↓) corresponds to $m_s = -1/2$, (anticlockwise). Method II is not common for giving the electronic configuration. It depicts certain features of the atom and its electronic configuration.

Some examples given below explain the Hund's rule explicitly. For example,

Boron (Z=5)	↑↓	↑↓	↑		
Carbon (Z=6)	↑↓	↑↓	↑	↑	

The 6th electron goes into a new 2*p* orbital.

Nitrogen (Z=7) ;	↑↓	↑↓	↑	↑	↑

The 7th electron also goes into a new 2p orbital. Thus, in nitrogen all the three 2p electrons are with parallel spins.

Oxygen (Z=8) ;	↑↓	↑↓	↑↓	↑	↑

The 8th electron must go into an orbital already occupied with an electron.

Fluorine (Z=9)	↑↓	↑↓	↑↓	↑↓	↑

The 9th electron goes into one of the two orbitals containing single electrons with parallel spins.

Neon (Z=10)	↑↓	↑↓	↑↓	↑↓	↑↓

With the 10th electron in the neon atom all the orbitals are fully occupied, and thus, the second principal energy level is filled.

The electronic configuration of potassium explains that in arriving at electronic configuration, the orbital with lower energy is always preferred over the orbital with higher energy.

Potassium (Z=19) ; $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$

The 19th electron for potassium, K enters the 4s orbital instead of 3d. This means that 4s orbital is at lower energy level than 3d. Similarly, we can have for calcium, *i.e.*,

Calcium (Z=20) ; $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3s^6$, $4s^2$

Since the first 18 electrons represent the configuration of argon,

the configuration of calcium can be written as, Ca ; [Ar] $4s^2$. Now the 21st electron will populate the 3d orbital. Thus,

Scandium (Z=21) [Ar] $4s^2$, $3d^1$..........

Although the last filled orbital for scandium, Sc is 3d, it is desired to place the sub-shells of each principal shell together

Thus, Sc ; [Ar] $3d^1$, $4s^2$.........

Similarly Zinc (Z=30) ; [Ar] $3d^{10}$ $4s^2$...........

STABILITY OF FILLED AND HALF-FILLED ORBITALS

Another factor that affects the ground state electronic configurations of certain atoms is the tendency for orbitals to become completely filled and exactly half-filled. For example, for chromium, Cr the electronic configuration is

Cr (Z=24) ; [Ar] $3d^5$ $4s^1$

Instead of Cr (Z=24) ; [Ar] $3d^4$ $4s^2$

This unexpected result occurs because a half-filled subshell possesses an extra added stability (*i.e.*, possesses lower energy).

Some other examples of this kind of deviation are :

Cu (Z=29) ; [Ar] $3d^{10}$ $4s^1$

Mo (Z=42) ; [Kr] $4d^5$ $5s^1$

In the case of copper, Cu the completely filled sublevel possesses extra stability. Another example of this kind of deviation using 5d and 4f levels is given below :

Gd (Z=64) ; (Xe) $4f^8$ $6s^2$
(Expected configuration)

Gd (Z=64) (Xe) $4f^7$ $5d^1$ $6s^2$
(Actual configuration)

Thus, in the case of Cr, Cu and Mo, the unexpected results are explained on the basis of the added stability of a completely filled or half-filled subshell. This concept of extra stability for half-filled and completely filled orbitals, is also seen in cases where the aufbau principle is followed. For example, N, P and As show unusual properties (*e.g.*, unusual high ionization potentials) because they all have half-filled p subshells. Similarly Zn, Cd and Hg show some unusual properties because they all possess completely filled subshells. Thus, the p^3, p^6, d^5, d^{10}, f^7 and f^{14} configuration which are either filled or half-filled are more stable.

In case of Gd and similar other cases (elements with higher atomic number), the variations are not because of the enhaneed stability of filled or half-filled subshells.

In conformity with the above rules and discussion, electron configurations of the elements are given in Table 1.4.

TABLE 1.4. Electron configurations of the elements

Atomic number	*Element*	*Electron configuration*
1	H	$1s^1$
2	He	$1s^2$
3	Li	[He] $2s^1$
4	Be	——$2s^2$
5	B	——$2s^2 2p^1$
6	C	——$2s^2 2p^2$
7	N	——$2s^2 2p^3$
8	O	——$2s^2 2p^4$
9	F	——$2s^2 2p^5$
10	Ne	$1s^2 2s^2 2p^6$
11	Na	[Ne] $3s^1$
12	Mg	——$3s^2$
13	Al	——$3s^2 3p^1$
14	Si	——$3s^2 3p^2$
15	P	——$3s^2 3p^3$
16	S	——$3s^2 3p^4$
17	Cl	——$3s^2 3p^5$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
19	K	[Ar] $4s^1$
20	Ca	——$4s^2$
21	Sc	——$3d^1 4s^2$
22	Ti	——$3d^2 4s^2$
23	V	——$3d^3 4s^2$
24	Cr	——$3d^5 4s^1$
25	Mn	——$3d^5 4s^2$
26	Fe	——$3d^6 4s^2$
27	Co	——$3d^7 4s^2$
28	Ni	——$3d^8 4s^2$
29	Cu	——$3d^{10} 4s^1$
30	Zn	——$3d^{10} 4s^2$
31	Ga	——$3d^{10} 4s^2 4p^1$
32	Ge	——$3d^{10} 4s^2 4p^2$
33	As	——$3d^{10} 4s^2 4p^3$
34	Se	——$3d^{10} 4s^2 4p^4$
35	Br	——$3d^{10} 4s^2 4p^5$
36	Kr	——$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
37	Rb	[Kr] $5s^1$
38	Sr	——$5s^2$
39	Y	——$4d^1 5s^2$

(Contd.)

(Contd.)

Atomic number	*Element*	*Electron configuration*
40	Zr	——$4d^2 5s^2$
41	Nb	——$4d^4 5s^1$
42	Mo	——$4d^5 5s^1$
43	Tc	——$4d^5 5s^2$
44	Ru	——$4d^7 5s^1$
45	Rh	——$4d^8 5s^1$
46	Pd	——$4d^{10}$
47	Ag	——$4d^{10} 5s^1$
48	Cd	——$4d^{10} 5s^2$
49	In	——$4d^{10} 5s^2 5p^1$
50	Sn	——$4d^{10} 5s^2 5p^2$
51	Sb	——$4d^{10} 5s^2 5p^3$
52	Te	——$4d^{10} 5s^2 5p^4$
53	I	——$4d^{10} 5s^2 5p^5$
54	Xe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
55	Cs	[Xe] $6s^1$
56	Ba	——$6s^2$
57	La	——$5d^1 6s^2$
58	Ce	——$4f^2 6s^2$
59	Pr	——$4f^3 6s^2$
60	Nd	——$4f^4 6s^2$
61	Pm	——$4f^5 6s^2$
62	Sm	——$4f^6 6s^2$
63	Eu	——$4f^7 5s^2$
64	Gd	——$4f^7 5d^1 6s^2$
65	Tb	——$4f^9 6s^2$
66	Dy	——$4f^{10} 6s^2$
67	Ho	——$4f^{11} 6s^2$
68	Er	——$4f^{12} 6s^2$
69	Tm	——$4f^{13} 6s^2$
70	Yb	——$4f^{14} 6s^2$
71	Lu	——$4f^{14} 5d^1 6s^2$
72	Hf	——$4f^{14} 5d^2 6s^2$
73	Ta	——$4f^{11} 5d^3 6s^2$
74	W	——$4f^{14} 5d^4 6s^2$
75	Re	——$4f^{14} 5d^5 6s^2$
76	Os	——$4f^{14} 5d^6 6s^2$
77	Ir	——$4f^{14} 5d^7 6s^2$
78	Pt	——$4f^{14} 5d^9 6s^1$
79	Au	——$4f^{14} 5d^{10} 6s^1$

(Contd.)

(Contd.)

Atomic number	*Element*	*Electron configuration*
80	Hg	—— $4f^{14}5d^{10}6s^2$
81	Tl	—— $4f^{14}5d^{10}6s^2 6p^1$
82	Pb	—— $4f^{14}5d^{10}6s^2 6p^2$
83	Bi	—— $4f^{14}5d^{10}6s^2 6p^3$
84	Po	—— $4f^{14}5d^{10}6s^2 6p^4$
85	At	—— $4f^{14}5d^{10}6s^2 6p^5$
86	Rn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$
87	Fr	[Rn] $7s^1$
88	Ra	—— $7s^2$
89	Ac	—— $6d^1 7s^2$
90	Th	—— $6d^2 7s^2$
91	Pa	—— $5f^2 6d^1 7s^2$
92	U	—— $5f^3 6d^1 7s^2$
93	Np	—— $5f^4 6d^1 7s^2$
94	Pu	—— $5f^6 7s^2$
95	Am	—— $5f^7 7s^2$
96	Cm	—— $5f^7 6d^1 7s^2$
97	Bk	—— $5f^8 6d^1 7s^2$
98	Cf	—— $5f^{10} 7s^2$
99	Es	—— $5f^{11} 7s^2$
100	Fm	—— $5f^{12} 7s^2$
101	Md	—— $5f^{13} 7s^2$
102	No	—— $5f^{14} 7s^2$
103	Lr	—— $5f^{14} 6d^1 7s^2$
104	(Ku)	—— $5f^{14} 6d^2 7s^2$
105	(Ha)	—— $5f^{14} 6d^3 7s^2$

PART II

1.10. CHEMICAL BONDING

Of the various forces of attraction, which can exist between atoms, the stronger ones are known as **chemical bonds.** You have already learnt about these chemical bonds and the molecules formed as a result of these bonds. Bonding is the key to molecular structure, and structure is intimately related to the physical and chemical properties of a compound. In class XI, we introduced some of the basic ideas of chemical bonding. Molecules are more stable than atoms, as they are formed with the evolution of energy.

Atoms can bond together in different ways :

By sharing electrons between atoms—covalent bonding.

By transferring electrons from one atom to another—ionic bonding.

By sharing electrons among all the atoms in the lattice—metallic bonding.

There exists other bonds such as, hydrogen bond and others.

Ionic bonds are the electrostatic attractions that exist between oppositely charged ions. Since ions are characterized by symmetrical positive or negative field, ionic bonds are non-directional.

Covalent bonding results from overlapping of atomic orbitals from different atoms and is followed by pairing of orbital electrons (valence bond theory). As a result, orbital electrons (with opposite spins) are centred in the region of overlap of atomic orbitals. In this region, the electron charge density (or probability) is quite high. The attraction of the nuclei for the shared electrons holds the atoms in a covalent bond. The strong bonds will be formed, if the atoms approach in such a way that there is maximum overlap between atomic orbitals. It follows that a covalent bond will have a preferred direction. A covalent molecule has a characteristic shape which is determined by the angles between the bonds joining the atoms together.

1.11. REVIEW OF VALENCE BOND METHOD

The valence bond (VB) method, developed by Linus Pauling (1930) with the help of wave mechanics is based upon the pairing and neutralization of spins of electrons. According to the VB point of view, a covalent bond consists of a pair of electrons shared between the bonded atoms. This means that two orbitals (one from each atom) must overlap in such a way that the electron pair simultaneously occupies both orbitals. This concentrates electronic charge in the region between the nuclei and so bonds the atoms together. This is the central tenet of valence bond theory, which describes how covalent bonding occurs. In many molecules the bonding is best described in terms of hybrid orbitals which are obtained from the mixing or combining of pure atomic orbitals. In the next section we shall treat covalent bonding by an alternate method, the **molecular orbital theory**. We shall also assume that each bonding pair and each lone pair occupies a separate orbital.

1.12. MOLECULAR ORBITAL THEORY IN CHEMICAL BONDING

In class XI, you have considered bonding and molecular geometry in terms of VB and of VSEPR theories respectively. In VB theory, electrons in overlapping orbitals of different atoms are thought of as being localized in the bonds between the two atoms

involved, rather than delocalized over the entire molecule. Molecular orbital theory, on the other hand, postulates the combination of atomic orbitals of different atoms to form **molecular orbitals**, so that electrons in them belong to the molecule as a whole. Both the theories have strengths and weaknesses that are complementary.

Molecular orbitals

The mathematical pictures of hybrid orbitals in VB theory can be produced by combining the wave functions that describe two or more atomic orbitals (ACs) on a single atom. Similarly the wave functions of AOs are combined mathematically to produce wave functions for the resulting MOs.* The number of new orbitals formed equals the number of original atomic orbitals combined.

For the effective overlap of atomic orbitals two conditions must be met: (*i*) the AOs must be of comparable energy, and (*ii*) they must overlap significantly. The quantum mechanical approach to the significant overlap consists of (*i*) an addition, and (*ii*) a subtraction of the AO wave functions. It is the ψ^2 for an electron gives the idea about the probability of finding that electron.

In case we treat MOs on these lines the probability-density pattern for the electrons in the molecule can be made available and hence the corresponding boundary surfaces (and also energy levels) can be obtained.

One linear combination of AOs is

$$\psi_{MO}=a\psi_A+b\psi_B \quad \ldots(1.9)$$

where *a*, *b* are the weighing factors related to the combination of each AO wave function to the MO wave function. For homonuclear molecule *a* and *b* are equal.

The electron probability function will be,

$$\psi^2_{MO}=(\psi_A+\psi_B)^2=\psi^2_A+2\psi_A\psi_B+\psi^2_B \quad \ldots(1.10)$$

Second possible linear combination of the two atomic orbitals is,

$$\psi^*_{MO}=\psi_A-\psi_B \quad \ldots(1.11)$$

for which the electron probability to function is

$$\psi^2_{MO}=(\psi_A-\psi_B)^2=\psi^2_A-2\psi_A\psi_B+\psi^2_B \quad \ldots(1.12)$$

The curve for ψ^2_{MO} in Fig. 1.20 shows that the electron density between nuclei increases by the term $2\psi_A\psi_B$ of equation (1.10). Similarly, the curve for ψ^2_{MO} in Fig. 1.20 shows that the electron density between nuclei separated by the bond length is decreased by the amount of the term $2\psi_A\psi_B$ of equation (1.12). The wave functions ψ^2_{MO} and ψ^{*2}_{MO} represent bonding molecular orbital and antibonding molecular orbital respectively. In bonding orbital, the electron charge density is concentrated in the region between the two nuclei. This decreases the repulsion effectively between the two nuclei and rather helps in holding the two atoms together. In the

*The method is known as the linear combination of atomic orbitals or LCAO method.

case of the anti-bonding orbital the electron charge density is concentrated outside the region between the two nuclei, which reduces the attraction between the atoms. Thus, the sum of ψ^2_{MO} and ψ^{*2}_{MO} in Fig. 1.20 is equal to the electron probability of the two AOs ψ^2_A and ψ^2_B; the attraction of the bonding orbital is cancelled by the repulsion resulting from the anti-bonding orbital.

The combination of wave functions discussed above may be compared with the combination of two waves of same wavelength and amplitude. If the two waves combine in phase (additive), the result is reinforcement and if they combine out of phase (subtractive), the result is cancellation of the waves.

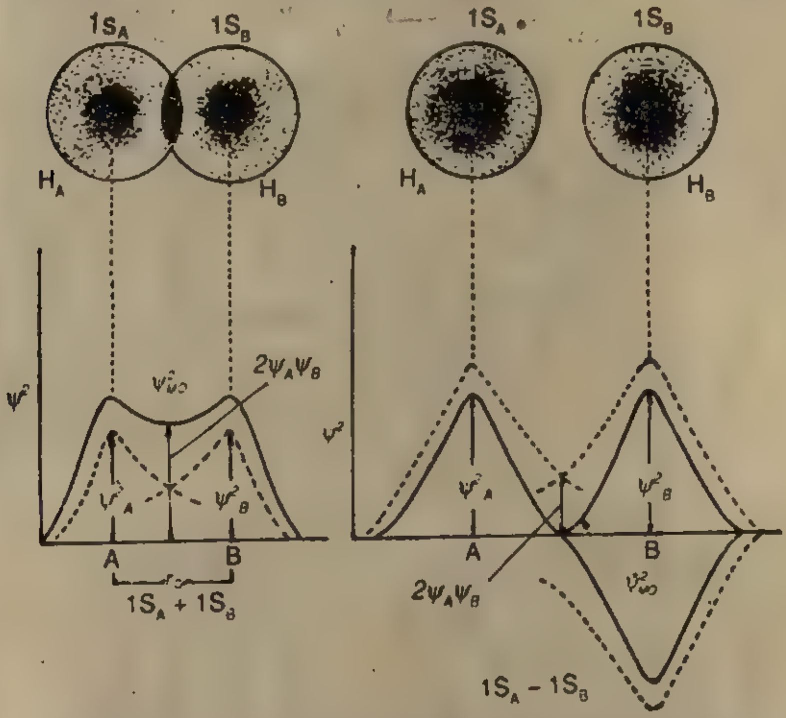


Fig. 1.20. Formation of the hydrogen molecule. (a) Constructive interference of the two wave functions lead to the concentration of electron density in the region between the nuclei. The solid line shows the increase in electron density, compared to two non-bonding atom, between the nuclei by the amount $2\psi_A\psi_B$. This additional electron density provides the attractive force holding the nuclei together (b) The solid line shows that the electron density is reduced by the amount $2\psi_A\psi_B$ in the anti-bonding orbital as a result of destructive interference of the two wave functions.

The bonding and anti-bonding orbitals for homonuclear diatomic molecules formed from specific atomic orbitals are designated as follows :

Bonding orbitals	*Anti-bonding *orbitals*	*Type of atomic orbitals used*
1s	σ^*1s	1s
2s	σ^*2s	2s
2p	σ^*2p_x	$2p_x$
$2p_y$	π^*2p_y	$2p_y$
$2p_z$	π^*2p_z	$2p_z$

The combination of various atomic orbitals in the valency shell

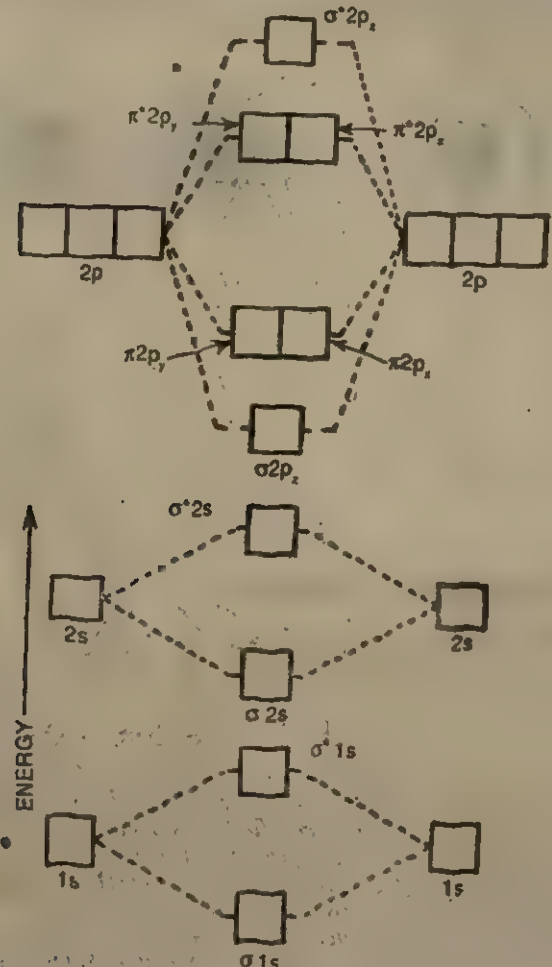


Fig. 1.21. Schematic molecular orbital energy diagram exhibiting the relative energies of molecular orbitals.

may be portrayed on a general energy level diagram as shown in Fig. 1.21. In building up the electronic structures of homonuclear diatomic molecules, the molecular orbitals follow a familiar pattern. Electrons tend to enter the lowest energy orbital, first singly and then in pairs (Hund's rule of maximum multiplicity). The orbitals are designated by the four quantum numbers n, l, m_l and m_s. Thus, each orbital will accommodate a pair of electrons. The two electrons in the molecular orbital will be of opposite spin to comply with the Pauli's exclusion principle. The relative energy sequence of molecular orbitals is as follows :

$\sigma 1s$, $\sigma^* 1s$, $\sigma^* 2s$, $\sigma^* 2s$; $\sigma 2p$, $\pi 2p_x$, $\pi 2p_y$, $\pi^* 2p_x$, $\pi^* 2p_y$, $\sigma^* 2p_z$ ($\pi 2p_x$ and $\pi 2p_y$ are of equal energy ; $\pi^* 2p_x$ and $\pi^* 2p_y$ are also of equal energy).

Note : For B_2, C_2 and N_2 the $\pi 2p$ orbitals are of slightly lower energy than $\sigma 2p$ orbital ; this is also true for Li_2 and Be_2 but in the ground state of these molecules the $\pi 2p$ and $\sigma 2p$ orbitals are, of course, all empty. This change in energy sequence is related to the 2s and 2p atomic orbitals. For the earlier members of the period (from Li → N), the energy for the 2s and 2p orbitals is almost the same, hence in addition to 2s—2s and $2p_z$—$2p_z$ interactions, 2s orbital can interact with $2p_z$ orbital.

1.12.1. Linear Combination of Atomic Orbitals

(A) Combination of s orbitals : On combining two 1s orbitals, two molecular orbitals result. Addition of overlap provides a bonding molecular orbital (Fig. 1.22). Subtraction of overlap gives an antibonding orbital (Fig. 1.22).

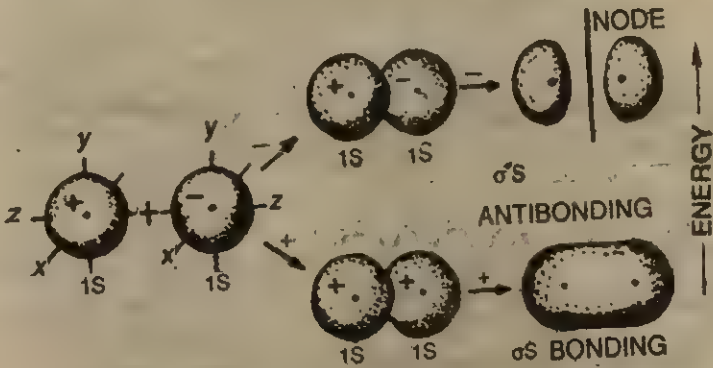


*Fig. 1.22. The combination of two 1s atomic orbitals to form σMOs : (a) bonding orbital (σ·1s) results from the symmetrical orbitals ; (b) antibonding orbital (σ·*1s) results from the antisymmetrical orbitals. Two atomic orbitals are with different algebraic signs.*

The resulting molecular orbitals are referred to as sigma (σs) orbitals.

In the case of antibonding orbital; there lies a nodal plane (plane of zero probability of finding the electrons) which is perpendicular to the line joining the nuclei at its mid-point (Fig. 1.22). The nodal plane removes electrons away from the bonding region between the nuclei and so the term antibonding is used. Thus, antibonding orbital (σ^*s) does not provide any bond. Electrons in antibonding orbitals cancel the bonding resulting from electrons in bonding orbitals.

The s orbitals are spherical in shape, and thus, charge is distributed symmetrically in all directions. They provide only σ-molecular orbital.

The molecular orbitals formed from the s orbitals from the different energy levels (2s, 3s, *etc.*) have the same characteristics but they are at a higher energy (Fig. 1.21).

(B) **Combination of** p **orbitals** : In dealing with the p atomic orbitals, it is necessary to take into account their orientation with respect to each other. If the two p orbitals from two atoms are assumed to line up along the internuclear axis (z-axis), then overlapping of the $2p_z$ orbitals produces σ-molecular orbitals (Fig. 1.23). The bonding orbital (σ-p_z) is formed if the overlapping lobes are chosen to have the same algebraic sign. The antibonding orbital (σ^*p_z) is formed if the algebraic sign in the overlapping lobes is different. This type of overlapping is called end-to-end. These molecular orbitals are symmetrical around the molecular axis (line joining the nuclei) and are also termed σ molecular orbitals by analogy with the symmetrical s atomic orbitals.

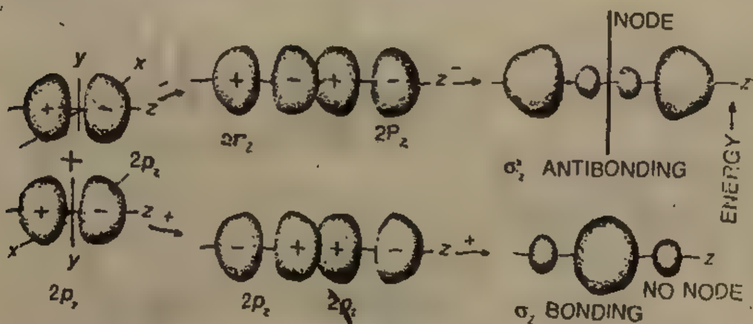


Fig. 1.23. The combination of two $2p_z$ *atomic orbitals to form σMOs*

The two p orbitals may also overlap laterally (parallel or side-by-side). Such p orbitals (say p'_z and p''_{xy}) cannot enter into σ bonding because they are antisymn[illegible] [illegible]hange in sign) across the

bond axis. Such orbitals combine to give bonding (πp) and antibonding (π *p) molecular orbitals (Fig. 1.24). Molecular orbitals have one nodal plane that passes through the two nuclei that are bonded. Because of the nodal plane, the electrons have a high probability of being on the two sides (above and below) of the plane (or bond axis). The antibonding molecular orbitals (π*p) have a nodal plane lying between the nuclei and is perpendicular to the line joining the nuclei at its mid-point (Fig. 1.24). This nodal plane keeps electrons out of the bonding region between the nuclei.

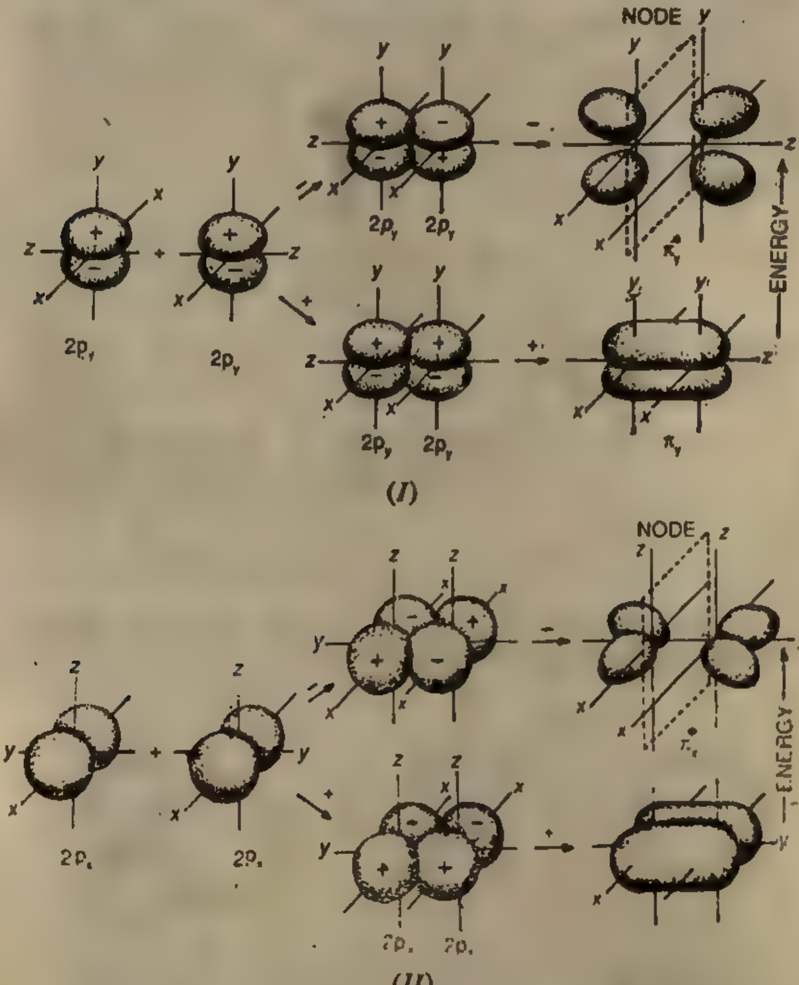


Fig. 1.24. The combination of two 2p atomic orbitals to form π MOs (I) π_y and (II) π_z

Since the p_x and p_y atomic orbitals are both perpendicular to the molecular axis and identical with each other apart from their orientation, they both form π orbitals in exactly the same way.

The π p_x and p_y molecular orbitals are equal in energy as are the π^*p_x and π^*p_y orbitals (Fig. 1.21). The πp interaction shows less effect on the electron density between the nuclei than the σp interaction. As a result, πp molecular orbitals do not differ much in energy compared to σp molecular orbitals.

All the σp and πp molecular orbitals from different energy levels have the same characteristics but differ only in energy.

(C) Combination of s **and** p **orbitals.** When an s orbital overlaps with a p_z orbital of comparable energy (directed along the bond axis, *i.e.* z-axis) a pair of new molecular orbitals (σsp) is formed (Fig. 1.25). Thus, two different atomic orbitals with the same symmetries about the bond axis give a bonding molecular orbital (σsp). The corresponding antibonding molecular orbital (σ^*sp) is also formed.

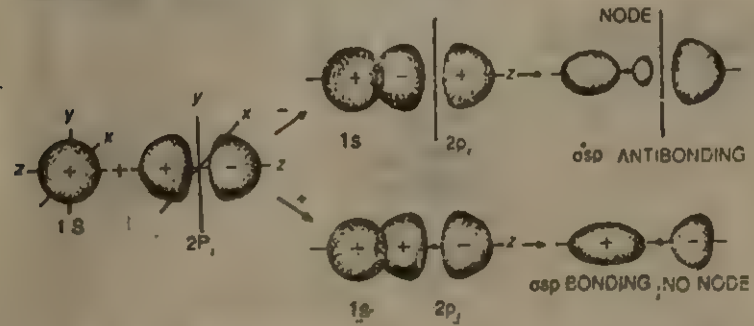


Fig. 1.25. The combination of one s *and one* p_z *orbital (effective overlap)*

Orbitals with different symmetries about the bond axis cannot overlap to give molecular orbitals (Fig. 1.26).

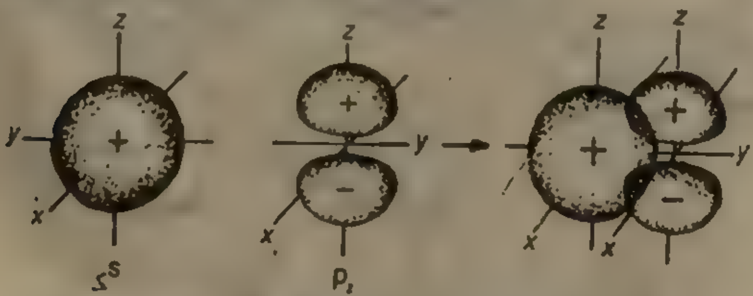


Fig. 1.26. Ineffective overlap of one s and one p *orbitals. Effect of plus-plus overlap is cancelled by plus-minus overlap.*

1.12.2. Stability and Bond Order

Number of electrons associated with both bonding and anti-bonding orbitals measure the stability of a molecule. If the number of electrons associated with bonding (X_b) orbitals exceeds the number of electrons associated with antibonding orbitals (X_a) the molecule is said to be stable. If X_a is greater than X_b, the molecule is unstable. If X_a is equal to X_b, the antibonding effect is stronger than bonding effect, hence, the molecule becomes unstable. Bond order is also a measure of the relative stability of molecules.

Bond order tells us about the number of bonds holding the two atoms together. A single bond is depicted by the bond order of 1. A bond order of 2 represents a double bond and a bond order of 3 represents a triple bond. It may be fractional also, *e.g.*, 1/2, 3/2, *etc.* The bond order is estimated by subtracting the number of electrons in the antibonding orbitals from the number of electrons in the bonding orbitals and dividing the difference by two.

Bond order of H_2 is 1 ; *e.g.*, $1/2\ (X_b - X_a) = (2-0)/2 = 1$

Bond order of He_2 is 0 ; *e.g.*, $1/2\ (X_b - X_a) = (2-2)/2 = 0$

The increase in bond order results in increase in bond strength and, therefore, increase in bond energy.

1.12.3. Formation of Diatomic Molecules and Ions

(A) First period elements. Four diatomic molecules and ions (H_2^+, H_2, He_2^+ and He_2) can be considered for the molecular orbitals formed from four electrons (from two 1s orbitals).

H_2 : Hydrogen molecule is made up of two hydrogen atoms, each of which possesses one electron in an 1s atomic orbital. When the two orbitals overlap, the two electrons from the atomic orbitals pair their spins and enter the molecular orbital (bonding orbital, σ1s) to give H_2 molecule. Figure 1.27 represents a molecular orbital

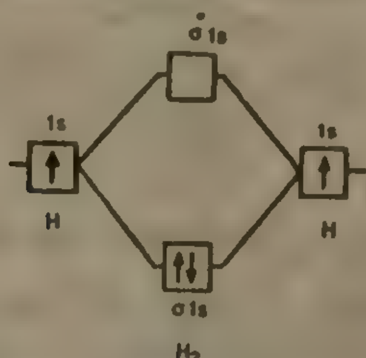


Fig. 1.27. Molecular orbital energy diagram for the hydrogen molecule.

energy diagram in which one electron within an orbital is represented by an arrow, $\boxed{\uparrow}$. Two electrons of opposite spins within an orbital are represented by $\boxed{\uparrow\ \downarrow}$

Similarly the molecular orbital energy level diagrams for H_2^+, He_2^+ and He_2 can be drawn [Figs. 1.28 (a), (b) and (c)].

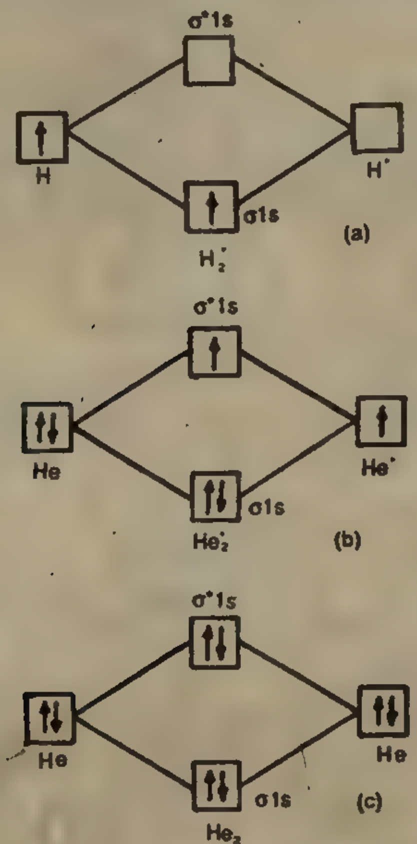


Fig. 1.28. Molecular orbital energy diagram : (a) H_2^+ ion, (b) He_2^+ ion, and (c) He_2.

H_2^+ : Dihydrogen ion is a single electron species. The electron enters the bonding orbital to produce H_2^+ ion. The net-energy of the ion is slightly lower than the energy of the hydrogen atom or of H^+ ion (one electron is present in bonding orbital and antibonding orbital is vacant). Hence, there is a strong tendency for hydrogen atom and a H^+ ion to combine to form H_2^+.

He_2^{2+} : Similar to H_2^+ ion, the dihelium ion (He_2^+) with three electrons (two electrons enter the lower energy molecular orbital in conformity with Hund's rules and the third electron enters the molecular orbital with higher energy, *i.e.* σ^*1s) would be expected to form.

He_2 : Dihelium molecule with four electrons would not be expected to form readily by the combination of two helium atoms. One pair of electrons in the bonding orbital would be balanced by the second pair of electrons in the antibonding orbital so no He_2 molecule would be formed from two He atoms. Thus, the net energy change would be zero depicting no tendency for helium atoms to combine to form He_2.

Stability, bond order and magnetic nature :

Based upon the foregoing discussion H_2, H_2^+, He_2^+ are stable and He_2 is not stable. The bond order for H_2, H_2^+, He_2^+ and He_2 is 1, $\frac{1}{2}$, $\frac{1}{2}$ and 0 respectively. H_2^+ and He_2^+ are paramagnetic* while H_2 is diamagnetic**. He_2 does not exist.

Now as bond order increases, bond length decreases and bond energy increases. Thus, the H_2 molecule is the most stable and the order of stability for these molecules or ions will be :

$$H_2 > H_2^+ = He_2^+ > He_2$$

He_2 molecule is non-existent, and thus, unstable which is in agreement with the theory of no bond. The experimental value for bond energy (bond energies ; $H_2 = 435$ kJ mol^{-1} ; $H_2^+ = 255$ kJ mol^{-1} ; $He_2^+ = 252$ kJ mol^{-1}) for these species also supports the order given above.

(B) Second period elements : In explaining the formation of diatomic molecules from the elements of second period elements, eight new molecular orbitals (because there are four orbitals in each atom—2s, $2p_z$, $2p_x$ and $2p_y$) are considered—four bonding and four antibonding. These orbitals follow the energy sequence given in Fig. 1.21. The differences of 2s orbitals from those of 1*s* and the two possibilities for the combination of p orbitals have been discussed in Section 1.12.1 : In the process of building up, we shall consider molecular orbitals arising from the second principal shell electrons (the first shell, K-shell electrons are not involved in bonding). The symbol 'KK' will be used to depict the electrons (not involved in the bonding) in the first electronic shell.

(*a*) **Li_2, Be_2, B_2 and C_2.** These diatomic molecules are not of any interest chemically. But they are being included for the sake

**Paramagnetic substance* : An atom, molecule or ion that has one or more electrons with unpaired spins and is attracted by a magnet.

***Diamagnetic substance* : An atom, molecule or ion that has no electrons with unpaired spins.

of completion. There are 6, 8, 10 and 12 valence electrons to be assigned to these molecules respectively.

Li_2, KK $\underset{\sigma 2s}{\boxed{\uparrow\downarrow}}$

BOND ORDER = 1 DIAMAGNETIC

Be_2, KK $\underset{\sigma 2s}{\boxed{\uparrow\downarrow}}$ $\underset{\sigma^* 2s}{\boxed{\uparrow\downarrow}}$

BOND ORDER = 0 DIAMAGNETIC

B_2, KK $\underset{\sigma 2s}{\boxed{\uparrow\downarrow}}$ $\underset{\sigma^* 2s}{\boxed{\uparrow\downarrow}}$ $\underset{\pi 2p_x}{\boxed{\uparrow}} = \underset{\pi 2p_y}{\boxed{\uparrow}}$

BOND ORDER = 1 ; PARAMAGNETIC

C_2, KK $\underset{\sigma 2s}{\boxed{\uparrow\downarrow}}$ $\underset{\sigma^* 2s}{\boxed{\uparrow\downarrow}}$ $\underset{\pi 2p_x}{\boxed{\uparrow\downarrow}} = \underset{\pi 2p_y}{\boxed{\uparrow\downarrow}}$

BOND ORDER = 2 DIAMAGNETIC

(*b*) N_2. The Lewis structure of nitrogen molecule

: N : : N : or : N≡N.

is confirmed by molecular orbital theory. There are fourteen electrons (each nitrogen atom contributes seven electrons) to be placed in molecular orbitals. According to energy sequence (Fig. 1·21) the arrangement of fourteen electrons that results is,

KK $\underset{\sigma 2s}{\boxed{\uparrow\downarrow}}$ $\underset{\sigma^* 2s}{\boxed{\uparrow\downarrow}}$ $\underset{\pi 2p_x}{\boxed{\uparrow\downarrow}} = \underset{\pi 2p_y}{\boxed{\uparrow\downarrow}}$ $\underset{\sigma 2p_z}{\boxed{\uparrow\downarrow}}$

Of the ten valence electrons (four electrons in KK are not involved in bonding), eight are in bonding orbitals and only two in an anti-bonding orbital (σ^*2s). The bonding provided by the filled $\sigma 2s$ is cancelled by the filled $\sigma 2s$. As a result of this cancellation a net of six bonding electrons are left, given by $\pi 2p_x$, $\pi 2p_y$ and $\sigma 2p_z$. These electrons signify a triple covalent bond confirming the Lewis structure for N_2.

N_2 is a diamagnetic molecule.

(*c*) O_2. There are sixteen electrons to be assigned to the various molecular orbitals. The filling of molecular orbitals is shown

in Fig. 1.29 (only 12 valence electrons are shown). The arrangement of electrons is,

$$\text{KK}\ \overset{\sigma 2s}{\boxed{\uparrow\downarrow}}\quad \overset{\sigma^* 2s}{\boxed{\uparrow\downarrow}}\quad \overset{\sigma 2p_z}{\boxed{\uparrow\downarrow}}\quad \overset{\pi 2p_x}{\boxed{\uparrow\downarrow}} = \overset{\pi 2p_y}{\boxed{\uparrow\downarrow}}\quad \overset{\pi^* 2p_x}{\boxed{\uparrow}} = \overset{\pi^* 2p_y}{\boxed{\uparrow}}$$

The total number of electrons in bonding orbitals is eight. The number of electrons in antibonding orbitals is four. According to MO description, the last two electrons have been accommodated in two separate antibonding orbitals (π^*2p_x and π^*2p_y) of the same energy in conformity with Hund's rule. Thus, the molecule has two unpaired electrons. This explains the known paramagnetic nature of O_2 (not predicted by Lewis structure, $:\ddot{O}::\ddot{O}:$, of O_2 rather predicts diamagnetic nature). The net of four electrons, excess of bonding over antibonding electrons, holds two atoms of oxygen together resulting into a double bond.

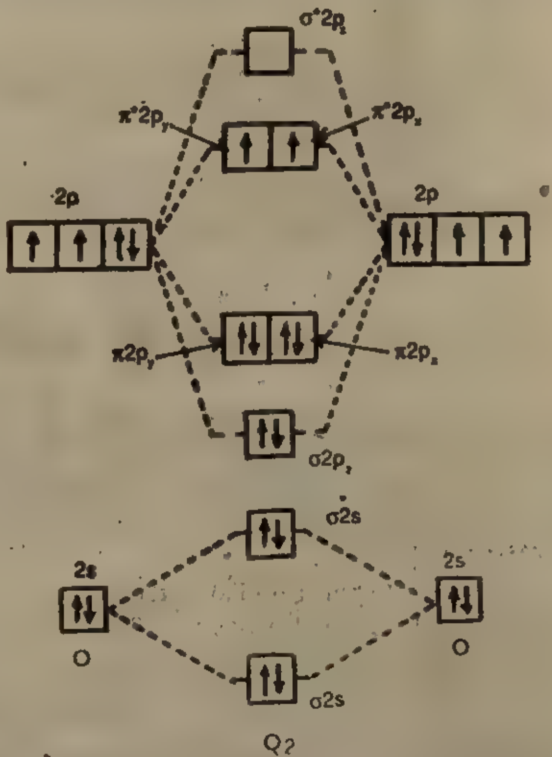
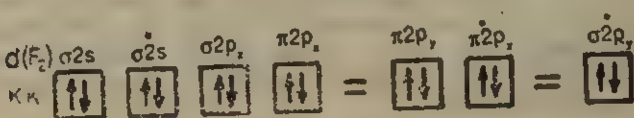


Fig. 1.29. Molecular orbital energy diagram for O_2 molecule.

The MO descriptions for other oxygen species, O_2^+, O_2^- and O_2^{2-} can be given either by simply adding electrons to or removing electrons from the MO description for O_2.

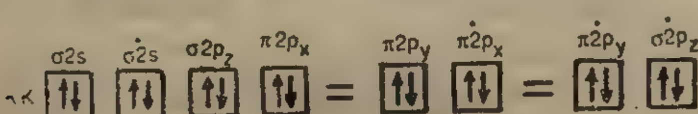
All the species are stable. The bond order for O_2^{2-}, O_2^+, O_2^- and O_2 is 1, 2.5, 1.5 and 2 respectively. O_2^+, O_2^- and O_2 are paramagnetic while O_2^{2-} alone is diamagnetic. The order of stability is : $O_2^+ > O_2 > O_2^- > O_2^{2-}$.

(*d*) **F_2**. The molecular orbital theory predicts that F_2 should be single bonded. Fluorine with 18 electrons has two extra electrons than O_2 molecule. The two singly occupied antibonding orbitals (π^*2p_x and π^*2p_y) in O_2 molecule are filled with two atoms additional electrons. Thus, F_2 has no unpaired electrons, *e.g.*,



Of the 14 valence electrons, there are eight electrons in bonding orbitals and six electrons in antibonding ones. Two bonding electrons lead to one covalent bond between two fluorine atoms confirming the Lewis structure for F_2.

(*e*) **Ne_2**. There are 20 electrons to be placed. They fill all of the ten orbitals (two from first energy shell and eight from second energy shell) available in the orbital scheme giving the pattern :

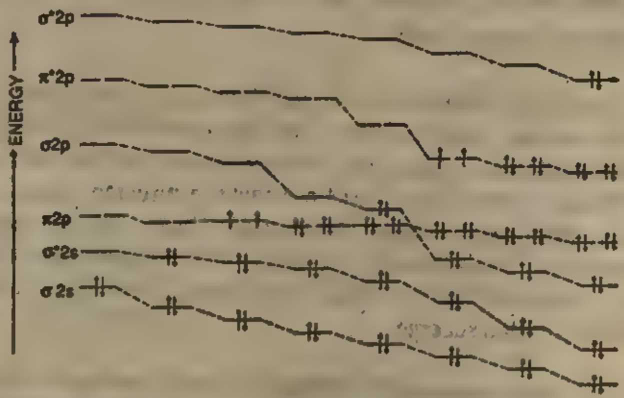


Ten of the electrons are in bonding orbitals, ten in antibonding orbitals, and hence, there is no bonding electrons to unite neon atoms together. Thus, the bond order will be zero and Ne_2 molecule will be unstable. There is no evidence that Ne_2 exists. Thus, molecular orbital theory confirms the monoatomic existence of neon gas.

In these ways, molecular orbital method answers the questions baffling the scientists earlier : if H_2 and F_2 form, why do not He_2 and Ne_2? They do not because in valence shell they have equal number of electrons both in bonding and antibonding orbitals. The theory also predicts the stability and magnetic nature of the various molecules. The ground state electron arrangement for homonuclear diatomic molecules and ions discussed above are summarized in Fig. 1.30. Molecular orbital theory can be extended to

cover heteronuclear diatomic molecules as well as polyatomic molecules.

Molecular orbital theory accounts for the bonding and geometry of many polyatomic molecules and complex ions. The MO approach to benzene molecule replaces the two contributing Lewis structures of resonance theory with three delocalized π orbitals on a σ bond framework. Certain wrong predictions revealed by valence bond theory about certain molecules have been predicted correctly (MO theory confirms the paramagnetic nature for O_2). Both valence bond and molecular orbital approaches are equally advantageous and neither can be considered superior to the other.



	Li_2	(Be_2)	B_2	C_2	N_2	O_2	F_2	(Ne_2)
BOND LENGTH/(pm)	267	—	159	124	110	121	142	—
BOND ENERGY/kJ mol^{-1}	110	—	272	602	941	493	139	—
BOND ORDER	1	0	1	2	3	2	1	0

Fig. 1.30. Electronic configuration of diatomic molecules.

1.13. HYBRIDIZATION OF ORBITALS

The use of pure atomic s and p orbitals has failed to account for the shape of most of the molecules. The description of simple atomic orbitals (s, p, d, *etc.*) is based on isolated atoms. The electronic arrangements for the isolated atoms are not applicable to bonded atoms. They have been successful in explaining some covalent bonds. The linear, trigonal, tetrahedral shapes for various molecules cannot be explained by using simple atomic orbitals and the idea of hybrid orbitals has to be introduced.

Covalent bonds have direction. The electronic orbitals of an uncombined atom can alter the shape and direction when that atom takes part in bond formation. In a molecule in which two or more

covalent bonds are present, molecular geometry is dictated by the bond angles about the central atom. The non-bonding electrons also affect the molecular geometry.

When 2s and three 2p orbitals combine they produce four identical hybrid orbitals at exactly the tetrahedral bond angles of 109°.28′. This type of mixing is called sp^3 hybridization. In CH_4, H_2O, NH_3, *etc.*, all the central atoms, *i.e.*, C, O and N undergo sp^3 hybridization before combining with H hydrogen atoms. In the process of hybridization, say for carbon atom in CH_4, some of the electrons are unpaired and promoted to vacant orbitals to account for various bonds.

Two other schemes of hybridization involving s and p orbitals are also possible. One s and one p orbitals give two identical sp hybrid orbitals. One s and two p orbitals produce three identical sp^2 orbitals. The two sp hybrid orbitals are directed along a straight line at a 180° angle. Both $BeCl_2$ and $HgCl_2$ can be explained by this scheme. The three sp^2 hybrid orbitals are directed in the same plane at angles of 120°. BF_3, NO_3^-, *etc.*, have been successfully explained by this scheme.

In many compounds d orbitals are also involved and can give rise to more complicated hybrid orbitals, *e.g.*, dsp^2, sp^3d and sp^3d^2 (Fig. 1.31). The involvement of d orbitals starts from third period elements. Both phosphorus and sulphur are from third period. Their electronic arrangements for the valence shell are $3s^2\,3p^3$ and $3s^2\,3p^4$ respectively. They form compounds like PF_3, PF_5, H_2S, SF_4, SF_6, *etc.* The structures of PF_3, and H_2S can be explained by sp^3 hybridization scheme (seen in NF_3 and H_2O). In explaining the stereochemistry of PF_5, SF_4 and SF_6 vacant d orbitals are used. Their counter compounds like NF_5, OF_4 and OF_6 are not known because both nitrogen and oxygen do not contain any vacant d orbitals to which electrons could be promoted to get the desired number of bonds.

(*a*) **dsp^2 hybridization.** The structure of $[Ni\,(CN_4)]^{2-}$ ion is square planar (Fig. 1.33). It acquires this structure from dsp^2 scheme of hybridization which can be suggested through orbital scheme given in Fig. 1.32.

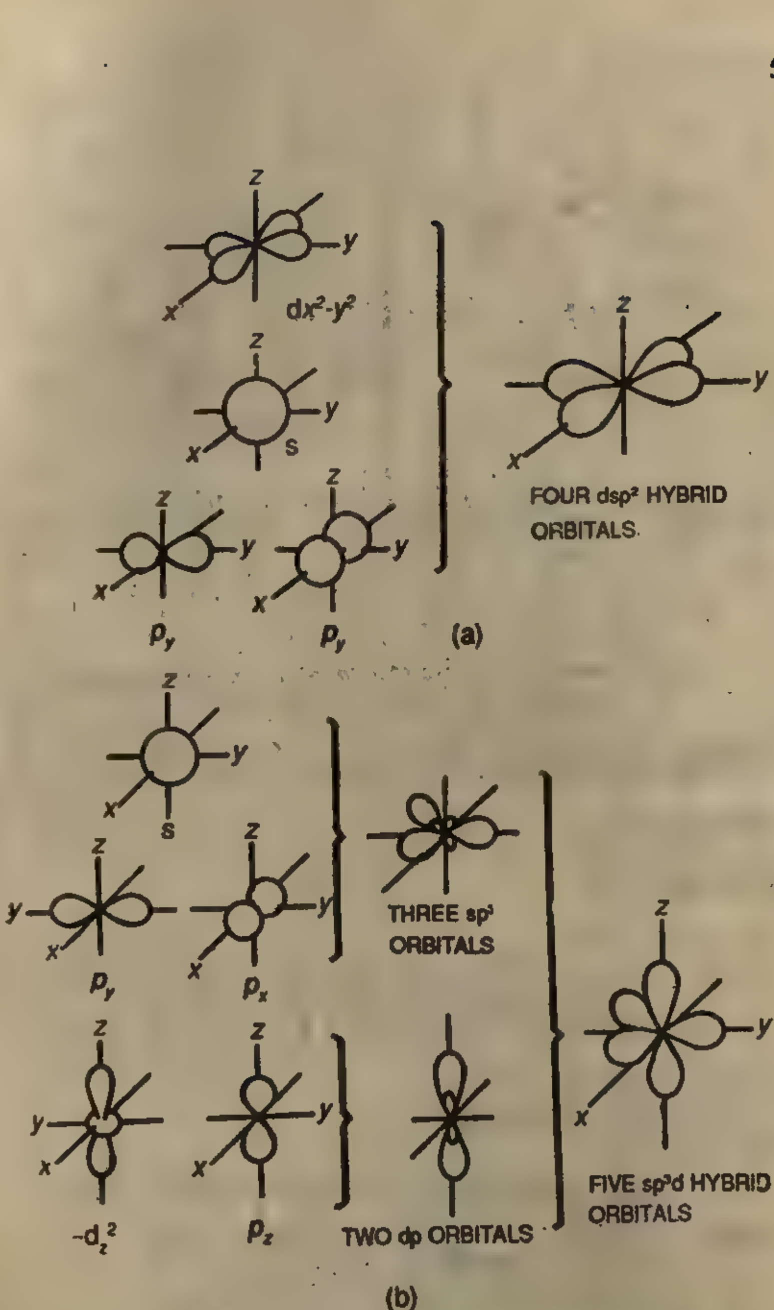


Fig. 1.31. (a) Mixing of orbitals to give four equivalent dsp^2 *hybrid orbitals. (b) Mixing of orbitals to give five* dsp^3 *or* sp^3d *hybrid orbitals.*

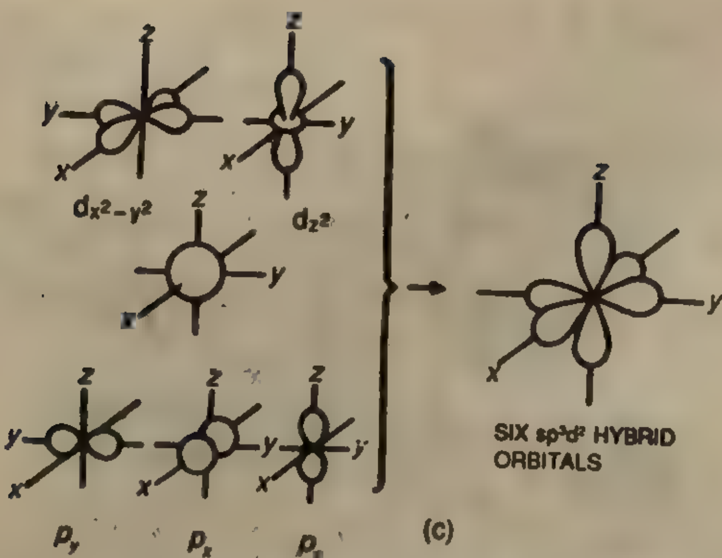
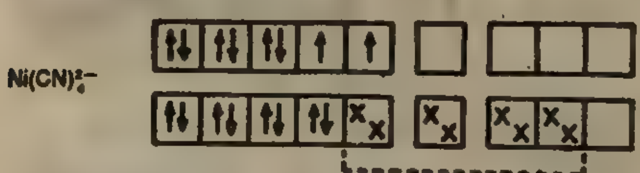


Fig. 1.31. (c) Mixing of orbitals to give six octahedrally disposed d^2sp^3 *or* sp^3d^2 *hybrid orbitals.*

GROUND STATE ELECTRONIC CONFIGURATION FOR NICKEL $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^8$ $4s$

GROUND STATE ELECTRONIC CONFIGURATION FOR VALENCE SHELL IN Ni $3d^8$ $4s^2$

GROUND STATE ELECTRONIC CONFIGURATION FOR VALENCE SHELL IN Ni^{2+}



(CROSSES REPRESENT ELECTRONS FROM CYANIDE IONS)

FOUR EQUIVALENT dsp^2 HYBRID ORBITALS

Fig. 1.32. Hybridization scheme for dsp^2

The dispositive nickel ion, Ni^{2+} has the electronic structure shown in Fig. 1.32. When bond formation occurs, the two d electrons with unpaired spin pair up under the influence of CN^- which is a strong ligand. In this process, one 3d orbital is made available for hybridization. The empty 3d orbital combines with the 4s and two 4p orbitals to form four *dsp*^{2} orbitals. Thus, the four bonding pairs of electrons occupy the four square planarly disposed dsp^2 hybrid orbitals (Fig. 1.33).

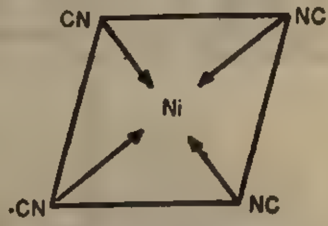


Fig. 1.33. Square planar structure of Ni $(CN)_4^{2-}$ *ion.*

The complex ions $[Pt(Cl)_4]^{2-}$ and $[Cu(NH_3)_4]^{2+}$ also adopt the dsp^2 hybridization.

(*b*) **sp^{3}d Hybridization :** The structure of PCl_5 is trigonal bipyramidal (Fig. 1.35). It arrives from sp^{3}d hybridization which can be envisaged as given in Fig 1.34.

It involves the promotion of electrons of the central atom to higher orbitals and then effecting hybridization. The five orbitals are not equivalent. There are two sets of equivalent hybridized orbitals. Three of these hybridized orbitals are oriented to the corners of an equilateral triangle at angles of 120° while the other set of two equivalent orbitals is perpendicular to the plane of the triangle, above and below it. These singly occupied hybrid orbitals overlap with p orbitals of five chlorine atoms to form PCl_5 molecule.

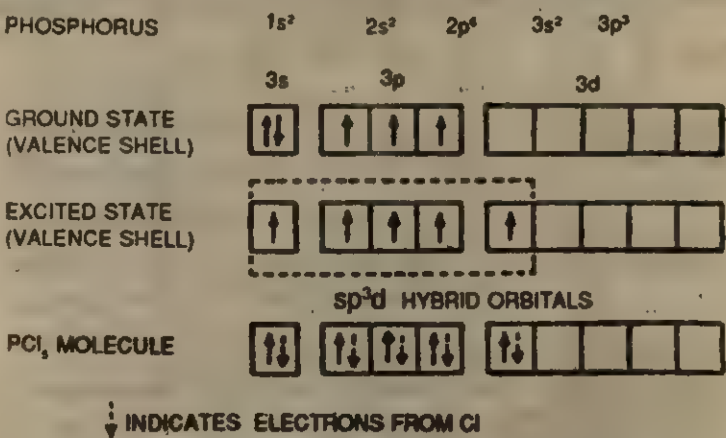


Fig. 1.34. Hybridization scheme for sp^{3}d.

SF_4 in its disposition also adopts sp^{3}d hybridization. In SF_4, the valence shell of sulphur atom contains four bonding pairs and

one lone pair of electrons. The five pairs are distributed around the corners of a trigonal bipyramid and the acceptable see-saw arrangement of the fluorine atoms about the sulphur atom is as shown in Fig. 1.36.

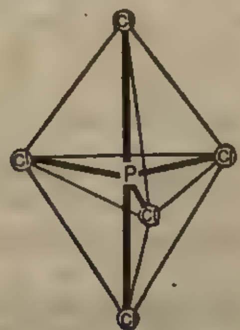


Fig. 1.35. Trigonal bipyramidal disposition for PCl_5

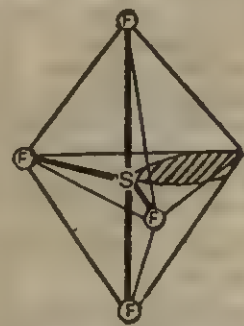


Fig. 1.36. Acceptable distribution of fluorine atoms and a lone pair of electrons in SF_4

(*c*) **sp^3d^2 Hybridization** : SF_6 is an octahedral molecule. Here each of the six bonds arises from the overlapping of fluorine p orbital with an sp^3d^2 hybrid orbital of the sulphur atom. These hybridized orbitals are oriented in space around the corners of a regular octahedron at angles of 90° (Fig. 1.38). For this octahedral molecule the hybridization can be envisaged as given in Fig. 1.37. Electrons from $3s^2$ and $3p_x^2$ orbitals of sulphur

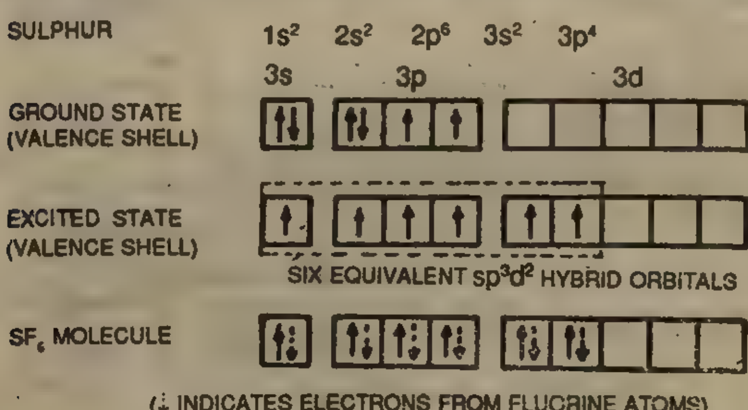


Fig. 1.37. Hybridization scheme for SF_6

are promoted to vacant 3d orbitals to make all the valence electrons unpaired. All the orbitals that are singly occupied are then

hybridized. The six sp^3d^2 hybrid orbitals overlap with p orbitals of six fluorine atoms to give SF_6.

Another example of sp^3d^2 hybridization is XeF_4. In XeF_4 there are four bonding and two lone pair of electrons in the valence shell of xenon. The disposition of XeF_4 is planar or octahedral with the apical positions occupied by two lone pairs.

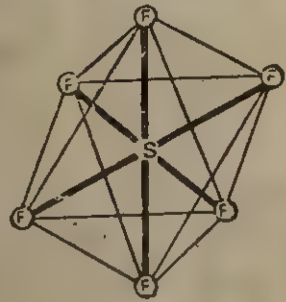
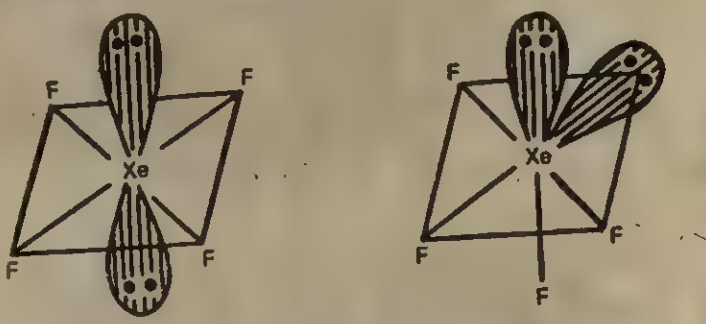


Fig. 1.38. Octahedral shape of SF_6

The possible arrangements of fluorine atoms about xenon atom are as shown in Figs. 1.39 (*a*) and (*b*). For the molecule to be stable the two lone pairs should occupy the apical positions. The repulsion is minimum between lone pairs when they occupy apical positions, *i.e.*, the lone pairs must be as far from each other as possible for there to be minimum repulsion (VSEPR). Thus, the arrangement (*a*) is preferable and the structure of xenon tetrafluoride is square planar. The directional nature of covalent bonds formed from the hybridized orbitals with examples of compounds is summarized in Table 1.5.



(*a*) (*b*)

Fig. 1.39. Possible distribution of fluorine atoms and two lone pairs of electrons.

1.14. BOND DISTANCE

In any covalent bond the average distance between the nuclei of the bonded atoms is called the bond distance or bond length. It is expressed in Å (or pm). The average bond distances of some bonds in molecules are given in Table 1.6. The actual bond length between atoms depends on the nature of atoms, the nature of bond between them, presence of lone pair of electrons, size of the atoms, environment of atoms, *etc*.

Table 1.5. Hybrid orbitals and their geometric orientation

Atomic orbitals	*Hybrid orbitals*	*Orientation*	*Bond angle*	*Geometry of the molecules formed*	*Examples*
s+p	sp	Linear	180°		$BeCl_2$, $HgCl_2$, C_2H_2
s+p+p	sp^2	Trigonal planar	120°		BF_3, BCl_3, NO_3^-, CO_3^{2-} C_2H_4, NO^-_2, SO_2, SO_3
s+p+p+p	sp^3	Tetrahedral	109°, 28′		CH_4, NH_4^+, BH_4^-, SiH_4, SO_4^{2-}, ClO_4^-, $SnCl_4$, ClO_3^-, ClO_2^-, ClO^-
d+s+p+p	dsp^2	Square planar	90°		$[Ni(CN)_4]^{2-}$ $[Cu(NH)_3]^{2+}$, $[PtCl_4]^{2-}$
s+p+p+p+d	sp^3d	Trigonal bipyramidal	120° and 90°		PCl_5, PF_5
s+p+p+p+d+d	sp^3d^2	Octahedral	90°		
d+d+s+p+p+p	d^2sp^3	Octahedral	90°		$[Co(NH_3)_6]^{3+}$, $[CrF_6]^{3-}$ SF_6 $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$

TABLE 1.6

Bond	*Bond length/ pm*	*Bond*	*Bond length/ pm*
H—H	74	H—Cl	136
Cl—Cl	198	C—H	109
C—C	154	C—Cl	177
C=C	133	O—Cl	96
C≡C	120	C—O	142

Bond length can be measured experimentally. Electron diffraction, X-ray techniques, and various spectroscopic methods are employed to determine the distances between atoms.

Let us consider the molecules H_2, Cl_2 and HCl. The bond lengths (r) in these molecules have been found to be

$$r\text{H—Cl} \quad 136 \text{ pm}$$
$$r\text{Cl—Cl} \quad 198 \text{ pm}$$
$$r\text{H—H} \quad 74 \text{ pm}$$

The bond length of HCl can be obtained by adding single bond covalent radius of hydrogen to that of chlorine. This is portrayed in Fig. 1.40.

$$r\text{HCl} = \tfrac{1}{2}\,(r\text{H}-\text{H}) + \tfrac{1}{2}(r\text{Cl}-\text{Cl})$$
$$= \frac{74}{2} + \frac{198}{2}$$
$$= 37 + 99 = 136 \text{ pm}$$

The relationship works well, however, only when the bonds are predominantly covalent. As the amount of ionic character in

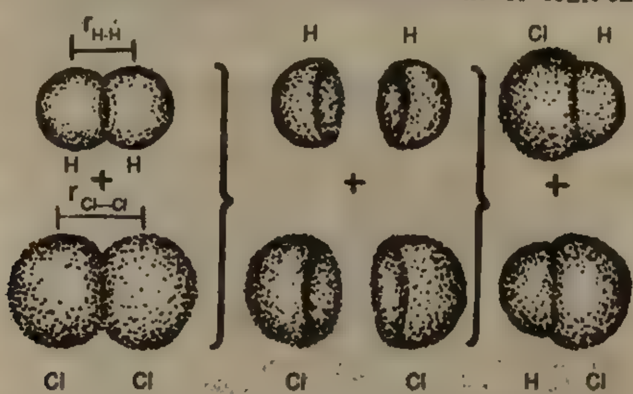


Fig. 1.40. Formation of two HCl molecules from combination of one hydrogen molecule and one chlorine molecule.

the bonds increases, the difference between the calculated and experimental values also frequently increases. In addition, hybridization effects and the multiplicity of bonds are important.

The C—C distance of 154 pm refers to a bond between two sp^3 hybridized carbon atoms, and the C=C distance of 133 pm refers to a bond between two sp^2 hybridized carbon atoms, whereas the C≡C bond (distance 120) generally occurs between sp hybridized carbon atoms.

Multiple bond radii are less than single bond radii. As a result, interatomic distances are less as the multiplicity of the bond increases. The double bonded radius for oxygen, as obtained from the oxygen molecule (60 pm) is larger due to repulsion effects than obtained from carbonyl compounds. The triply bonded radius of nitrogen is about the same if obtained from the N_2 molecule as from HCN or other molecules containing triply bonded nitrogen. In N_2 molecule the repulsion effects are not very effective due to the presence of only a single lone pair of electrons which is situated at an angle of 180° to the bonding electrons. Table 1.4 gives single and multiple bond radii of atoms.

TABLE 1.7. Single and multiple covalent bond radii of some atoms

Single bond radius/pm				*Multiple bond radius*/pm	
H	37	P	110	C	=67
K	77	O	66	C	≡60
Si	117	S	104	N	≡55
N	70	F	64	O	=55 (60)
B	82	Cl	99	N	=60
Al	118	Br	114	S	=94
		I	133	P	=100

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

1.1 Choose the correct answer of the four alternatives given for the following questions :

(*i*) The shape of the orbital is governed by..............quantum number.

(*a*) principal (*b*) azimuthal

(*c*) magnetic (*d*) spin

(*ii*) For a given value of azimuthal quantum, l the number of allowed values of the magnetic number m_l is given by

(*a*) $2l+1$ (*b*) $2l+2$

(*c*) $l+1$ (*d*) $l+2$

(*iii*) Which of the following sets of quantum numbers is not allowed ?

(*a*) $n=2$ $l=1$ $m_l=-1$ (*b*) $n=2$ $l=0$ $m_l=0$

(*c*) $n=2$ $l=0$ $m_l=+1$ (*d*) $n=2$ $l=1$ $m_l=+1$

(*iv*) Planck's equation is

(*a*) $E=mc^2$ (*b*) $\lambda=\frac{h}{p}$

(*c*) $\Delta p\ \Delta x \geqslant \frac{h}{4\pi}$ (*d*) $E=h\nu$

(*v*) Photoelectric effect is an example of

(*a*) wave nature of light (*b*) wave nature of electrons

(*c*) particle nature of light (*d*) None

(*vi*) At a fixed velocity, which of the following will have the highest wavelength ?

(*a*) positron (*b*) neutron

(*c*) proton (*d*) electron

(*vii*) The probability of finding the electron on the nucleus is

(*a*) finite for all orbitals. (*b*) zero for all orbitals.

(*c*) infinite for all orbitals. (*d*) finite only for s orbital.

(*viii*) The number of molecular orbitals obtained by mixing one atomic orbital from each of the two atoms is

(*a*) 4 (*b*) 3

(*c*) 2 (*d*) 1

(*ix*) Phosphorus in PCl_5 involves

(*a*) dsp^2 orbitals (*b*) sp^3d orbitals

(*b*) sp^3d^2 orbitals (*d*) sp^3 orbitals

(*x*) Which of the following species has two unpaired electrons in their molecular orbitals ?

(*a*) O_2 (*b*) O_2^+

(*c*) O_2^- (*d*) O_2^{2-}

1.2. Fill in the blanks with appropriate words :

(*i*) The German scientist.........pointed to the fact that exact knowledge of the position of an electron and its.........cannot be accurately determined at the same time.

(*ii*) For a hydrogen atom, the 1s electron is considered having one node at the nucleus, the other at.........

(*iii*) The probability of p electron at or very near the nucleus is almost.........

(*iv*) Energy associated with molecular orbitals after like atoms combine is.........initial atomic orbitals.

(*v*) The charge cloud diagrams show that an............does not have a rigid.........

(*vi*) The value of R works out to be.........J mol^{-1}.

(*vii*) The molecular orbital model permits calculation of.........and production of the.........and number of.........in a species.

(*viii*) Molecular orbital theory considers that valence shall.........cease to exist when a molecule is formed.

(*ix*) A.........bond is characterized by two regions.........on opposite sides of the bond axis.

(*x*) Sulphur hexafluoride molecules, SF_6 are.........and.........with no lone pair of electrons on the sulphur atom.

1.3 Which of the following statements are true and false. Write (T) or (F) against each :

(*i*) A magnetic field exerts no force on a stationary electron

(*ii*) The wavelength of visible light is smaller than that of X-rays.
(*iii*) When $l=3$, m_l may have integral values ranging from -3 to $+3$.
(*iv*) If ψ is the wave function for a particle, then ψ^2 represents the probability of finding the electron.
(*v*) A region in which the probability of finding an electron is maximum is called nodal plane.
(*vi*) In VB theory the atomic orbitals overlap in such a way that the electron pair simultaneously occupies both the orbitals.
(*vii*) A wave equation is an algebraic equation.
(*viii*) The $3d_{xy}$ orbital consists of four lobes, each of which is located along the x and y coordinate axes.
(*ix*) Two electrons in a given atom can be in exactly the same state.
(*x*) The principal quantum number, n specifies the total number of nodes in the charge cloud.

1.4 Match the following choosing one item from column X and the appropriate item from column Y

Column X	*Column Y*
(*i*) Azimuthal quantum number, l	(*a*) Electron probability is zero
(*ii*) xz plane	(*b*) Diffraction of electrons
(*iii*) de Broglie	(*c*) sp^3d
(*iv*) G.P. Thomson	(*d*) Orbital shape
(*v*) Electromagnetic waves	(*e*) See-saw shape
(*vi*) Oxygen molecule	(*f*) Wave-like properties of electron
(*vii*) PF_5 molecule	(*g*) Behave like particles
(*viii*) SF_4	(*h*) Addition of AOs
(*ix*) Bonding MO	(*i*) Subtraction of AOs
(*x*) Antibonding MO.	(*j*) Paramagnetic

SHORT ANSWER QUESTIONS

1.5 (*i*) What is the orbital hybridization in each of the species : BeH_2, H_3O^+, $SnCl_2$, ICl_4^-, SF_4 ?
(*ii*) Compare the bond order, bond length and bond energy in O_2, O_2^+, O_2^-, O_2^{2-}. Which of these are paramagnetic ?
(*iii*) What is the shape of orbitals for which $l=0$? Those for which $l=1$?
(*iv*) In the ground state of Ar, how many electrons have $m_l=+1$ among their quantum numbers.
(*v*) For N_2, $\pi 2p_x$ and $\pi 2p_y$ MOs are of lower energy than $\sigma 2p_z$. Comment.
(*vi*) What designations are given to orbitals having
(*a*) $n=2$, $l=1$; (*b*) $n=2$, $l=0$;
(*c*) $n=4$, $l=3$; (*d*) $n=4$, $l=2$;
(*e*) $n=4$, $l=1$.
(*vii*) How many orbitals are present in each of the following sub-levels ? Give their types.
(*a*) $l=2$ (*b*) $l=0$
(*c*) $l=1$
(*viii*) What is the difference between an orbit and an orbital ?

(*ix*) What shapes are associated with each of the species ?
ClF_3 SF_6, XeF_2, BF_3

(*x*) What is the maximum number of electrons that can occupy a molecular orbital ?

TERMINAL QUESTIONS

1.1 Describe, in brief, the wave particle duality as advanced by de Broglie. Give the expression relating the particle and wave nature of an object.

1.2 What are the main features of quantum mechanical model of atom ? Is it an improvement over particle model ?

1.3 What are quantum numbers ? Describe these in terms of their significance.

1.4 Comment on the introduction of magnetic quantum number and magnetic spin quantum number.

1.5 A number of apparent exceptions occur to the expected order of filling the electron orbitals. Explain why this is so ?

1.6 Discuss the following terms ; electron cloud, probable electron density, atomic orbital.

1.7 Show how the Bohr theory of the atom is inconsistent with the Heisenberg uncertainty principle.

1.8 If all the particles have wave-like properties, why is that diffraction of large particles such as base-balls and bullets is not observed ?

1.9 Using probability-density curves show that a 2p electron is less strongly bound to the nucleus than a 2s electron.

1.10 Compare the shapes of the orbitals in each of the following pairs :
(*a*) 1s and 2s (*b*) 2p and 3p.

1.11 (*a*) Every atomic orbital has a node at infinity. Explain.
(*b*) The probability of finding a 1s and 2s electron is the highest at the nucleus in each case. Explain.
(*c*) If the statement in (*b*) is correct, is it correct to say that the 2s subshell is farther from the nucleus than the 1s subshell. Explain.

1.12 (*a*) How are the possible values for azimuthal quantum number, l for a given electron restricted by the value of n ?
(*b*) How are the values of m_l for a particular electron restricted by the value of l ?

1.13 (*a*) The probability of finding an electron at any point is directly proportional to the electron density at that point. Explain the meaning of the statement.
(*b*) The highest energy electron of a lithium atom in its ground state is in the 2s orbital. Explain the meaning of the statement.

1.14 What do you understand by the term molecular orbital ? What is the method of LCAO to build a molecular orbital ? How does it differ from the valence bond method ?

1.15 Explain the following :
(*a*) Molecular orbitals formed are of lower energy than atomic orbitals.
(*b*) Nature of molecular orbitals depend upon the algebraic signs of the atomic orbitals.
(*c*) There is a large buildup of electron density between the two atoms which bonds them together.
(*d*) Two p orbitals overlap in different ways.

(e) An antibonding orbital is always at a higher energy than its corresponding molecular orbital.
(f) Antibonding orbital, σ^*1s is lower in energy than bonding orbital, $\sigma 2s$ yet it does not hold two atoms together. Why?
(g) Be has no unpaired electrons but it forms BeF_2.
(h) Both NCl_3 and BCl_3 have same number of covalent bonds but they adopt different geometry.
(i) The bond distances for N_2, N_2^+, O_2 and O_2^+ are : 109 pm, 112 pm, 121 pm and 112 pm respectively.

1.16 What shapes are associated with the following hybridizations? Give two examples of each sp, sp^2, sp^3, dsp^2, sp^3d, sp^3d^2.

1.17 Explain the following :
(a) F_2 molecule is less stable than N_2.
(b) Ne_2 is unstable.
(c) Extent of overlapping is a measure of bond strength.
(d) Bond order is the measure of stability of a molecule.
(e) N_2 has greater dissociation energy than N_2^+ whereas O_2 has a lower dissociation energy than O_2^+.

1.18 (a) All the bond lengths and bond angles in CH_4 and SF_6 are equal whereas in PF_5 there exists two sets of bond lengths and bond angles. Explain.
(b) Explain why two hydrogen atoms combine to form H_2 while helium remains monoatomic.
(c) Show that oxygen is paramagnetic.
(d) Why are the π bonds in N_2 different in energy from the σ bond?

1.19 (a) Which of the following species have sp^2 and sp^3 hybridizations? NH_3, NO_3^-, CF_4, BF_3, BeF_2, SO_2, SO_3, SO_3^{2-} and SO_4^{2-}
(b) Why are the bond angles in CH_4 and SiH_4 the same?
(c) All the three atomic p orbitals are of the same energy but the molecular orbitals formed from them are not of the same energy. Explain.

1.20 (a) Describe molecular orbital theory.
(b) Draw diagrams showing the molecular orbitals that result from combination of s atomic orbitals; combination of p atomic orbitals. Indicate the types of bond formed.

1.21 (a) Give the energy level diagram for the various molecular orbitals for homonuclear diatomic molecules.
(b) Compare atomic orbitals and molecular orbitals; bonding orbitals and antibonding orbitals; σ orbitals and π orbitals.

1.22 (a) What property do σ orbitals formed from two s atomic orbitals and σ orbitals formed from two 'end-to-end' p atomic orbitals have in common?
(b) Would you expect that σ molecular orbital could be formed from an s atomic orbital on one atom and a p orbital on a second?
(c) How are the following related to one another : (i) stability of a diatomic molecule, (ii) its dissociation energy, and (iii) its bond order?

1.23 Predict the hybridization and geometry of each of the following molecules : PF_5, CCl_4, $SiCl_4$, and $PbCl_2$. Explain your conclusions.

1.24 Distinguish between hybrid orbitals and molecular orbitals, with respect to : (i) the number of orbitals involved, (ii) the number of orbitals pro-

duced from a given number of ground state orbitals, and (*iii*) the energies of the resulting set of orbitals with respect to each other.

1.25 Draw the suitable molecular orbital diagrams for three different molecules in which single, double and triple bonds are possible.

ANSWERS TO SELF ASSESSMENT QUESTIONS

1.1 (*i*) a (*ii*) a (*iii*) c (*iv*) d (*v*) c
(*vi*) d (*vii*) a (*viii*) c (*ix*) b (*x*) a

1.2 (*i*) Heisenberg, momentum (*ii*) infinity
(*iii*) zero (*iv*) less than or greater than
(*v*) orbital, boundary/size (*vi*) $-1{\cdot}312\times10^6$
(*vii*) orbital energies, bond order, unpaired electrons
(*viii*) atomic orbitals. (*ix*) $\pi(p\pi)$, high electron density
(*x*) octahedral, nonplanar

1.3 (*i*) T (*ii*) F (*iii*) T (*iv*) T
(*v*) F (*vi*) T (*vii*) T (*viii*) F
(*ix*) F (*x*) T

1.4 (*i*) d (*ii*) a (*iii*) f (*iv*) b
(*v*) g (*vi*) j (*vii*) c (*viii*) e
(*ix*) h (*x*) i

1.5 (*i*) BeH_2, sp ; H_3O^+, sp^3 ; $SnCl_2$ sp^2 ; ICl_4, sp^3d^2 ; SF_4, sp^3d
(*ii*) Bond order O_2^+ (2·5), O_2 (2), O_2^- (1·5), O_2^{2-} (1)
Bond length $O_2^{2-} > O_2^- > O_2 > O_2^+$
Bord energy $O_2^+ > O_2 > O_2^- > O_2^{2-}$
Paramagnetic O_2^+, O_2, O_2^-
(*iii*) $l=0$ spherical ; $l=1$, dumb-bell
(*iv*) 4 electrons
(*v*) In nitrogen, the 2s and 2p orbitals lies sufficiently close that in addition to 2s—2s and $2p_z-2p_z$ interactions, the 2s orbital can interact with the $2p_z$ orbital. Interaction between the 2s and $2p_y$ or $2p_x$ orbitals results in no net effect, however, since this combination results in both bonding and antibonding effects. The $2s-2p_z$ interaction stabilizes the $\sigma 2s$ and $\sigma^* 2s$ orbitals, *i.e* , lowers their energy, at the expense of the $\sigma 2p_z$ and $\sigma^* 2p_z$ orbitals. The result is that the energies of the latter two orbitals are raised, so that the $\sigma 2p_z$ orbital lies above the $\pi 2p$ orbitals producing a different aufban order for the MOs.
(*vi*) (*a*) 2p (*b*) 2s (*c*) 4f (*d*) 4d (*e*) 4p
(*vii*) (*a*) 5, d orbitals (*b*) 1, s orbital
(*c*) 3, p orbitals.
(*viii*) **Orbit** : a well defined path or trajectory around the nucleus in which electrons are expected to move. This term was introduced by Bohr
Orbital : a region around the nucleus in which there is a maximum probability of locating the electron.
(*ix*) ClF_3 T shape ; SF_4—see-saw ; XeF_2—linear ; BF_3—Trigonal.
(*x*) Two electrons as permitted by Pauli's exclusion principle.

□□

UNIT 2

The Solid State

The infinite variety in the properties of solid materials we find in the world is really the expression of the infinite variety of the ways in which the atoms and molecules can be tied together and of the strength of those ties.

—*WILLIAM BRAGG*

UNIT PREVIEW

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Describe the nature of the crystalline state and the different unit cells from which the crystal lattice can be constructed.
2. Discuss the structure of some ionic compounds.
3. Describe the close packing arrangements of uniform size spheres and different size ions.
4. Comment on ionic radii.
5. Describe the classification of silicates on the basis of arrangement of basic units, SiO_4.
6. Describe the various types of imperfections come across in the crystal lattice.
7. Comment on the impurity defects as point defects.
8. Describe the properties of solids.
9. Describe the amorphous solids and compare them with crystalline solids.

2.1. INTRODUCTION

Solids are relatively hard, unyielding substances with a tendency to form, or be found as, crystals. The properties of solids depend upon the bonding forces between the particles at the lattice points of the crystal. These forces can be ionic bonds, covalent bonds, metallic bonds or van der Waals forces. In class XI, we have already examined about this aspect of the solids. We shall now turn our attention to the properties of crystalline solids by pursuing

answers to the following questions : What properties are characteristic of solids ? How are the properties of solids related to their structures ? In this unit, we shall also examine certain aspects of the structure of silicates and of amorphous solids.

2.2. STRUCTURE OF SOME SIMPLE IONIC COMPOUNDS

Ionic compounds form crystals in which the units making up the lattice are ions. The forces holding the crystal together are the electrostatic attractions between ions of opposite charges. In these compounds, each positive ion is surrounded by negative ions and vice versa. No particular positive ion belongs to any particular negative ion ; there is no molecule as such, the problem of ionic structures therefore differs in three ways from those considered earlier (in Class XI).

1. The problem is obviously no longer that of the packing of identical spheres but rather the mutual packing of two (or more) different species of units.
2. The stoichiometry of the compound may be other than 1 : 1, so that the crystal may contain different numbers of the various kinds of units.
3. The third problem is that there is a limit to the number of units of a given size which can be placed in contact with a smaller unit without their getting in each other's way.

Since the ions in an ionic lattice are not free to move, they vibrate about their fixed positions. Because of this property, ionic solids are poor electrical and thermal conductors. However, molten salts are excellent conductors because their ions are freely mobile.

We shall consider the more common types of crystal lattice for compounds of stoichiometry AB and AB_2. A and B can represent not only simple ions, for example K^+ and Cl^-, but also more complex ions such as NH_4^+, SO_4^{2-} or SiF_6^{2-}. Most salts of the AB type are cubic and crystallize in one of three kinds of lattices shown in Figs 2.1, 2.2, 2.5 and 2.6.

Rock Salt Structure

Rock salt has a face centred lattice with chloride ions of the lattice points and sodium ions at the cube centre and the mid-points of the cube edges (Fig. 2.2). By counting the number of Cl^- ions that are closest to the Na^+ ion in the centre of the unit cell, we can see that the co-ordination number of Na^+ is 6 and this ion occupies an octahedral hole defined by the six nearest Cl^- ions. The Na^+ ion is sufficiently large to prevent the Cl^- ions touching each other, and at the same time allows efficient packing so that the electrostatic forces of attraction are large. Figure 2.3 (*a*) portrays the packing of Na^+

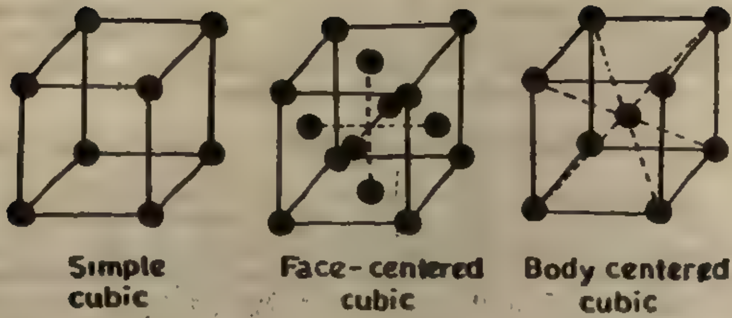


Fig. 2.1. Three possible unit cells of a cubic system.

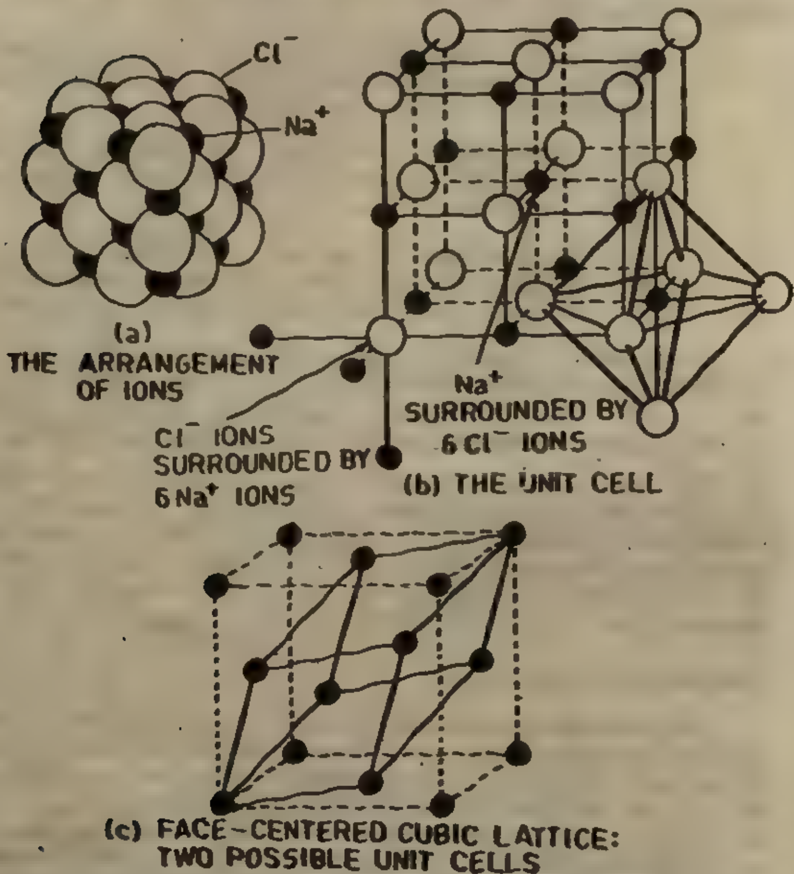


Fig. 2.2. Rock salt structure: (a) the arrangement of ions, (b) the unit cell, and (c) face centred cubic arrangement—two possible unit c.lls.

and Cl^- ions in a layer of NaCl, where four Cl^- ions surround each Na^+ ion and four Na^+ ions surround each Cl^- ions.

Identical layers are seen in the horizontal and vertical planes at right angles to each other so that, in the crystal lattice, each ion is surrounded by six oppositely charged ions [Fig 2.3 (b) and (c)]. Each sodium or chloride ion has a co-ordination number of six. The surrounding ions form an octahedron and the centres of the surrounding ions are at the corners of a regular octahedron. Further, each surrounding ion say Cl^- is at the centre of an octahedron of Na^+ ions. Each ion, thus, has a co-ordination number of six and the rock salt structure to possess 6 : 6 co-ordination. Sodium chloride may also be described as two interpenetrating, identical, face centred cubic lattices, one of Na^+ and the other of Cl^- ions. Examination of Fig. 2.2 (c) reveals that the ions occupy the corners of a cube and also the centres of each face of the cube. At ordinary temperatures and pressures, chlorides, bromides and iodides of Li, Na, K and Rb and also some of the halides of silver possess the rock salt structure. They adopt CsCl structure at high pressure.

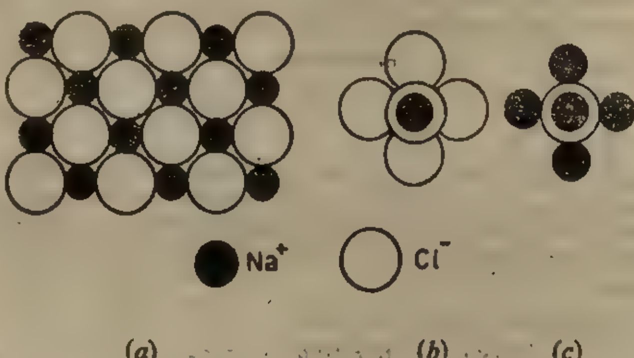


Fig. 2.3. Packing of Na^+ and Cl^- ions in NaCl : (a) represents a layer of the structure, (b) and (c) represent the 6 : 6 co-ordination of the structure.

We know that the relative sizes of the ions and also the numbers of anions and cations determine the nature of lattice and structure of the ionic crystal. Since a crystal is built up of a large number of unit cells, whatever the anion/cation ratio is in the crystal as a whole, it must also be the same in the unit cell. On counting the number of

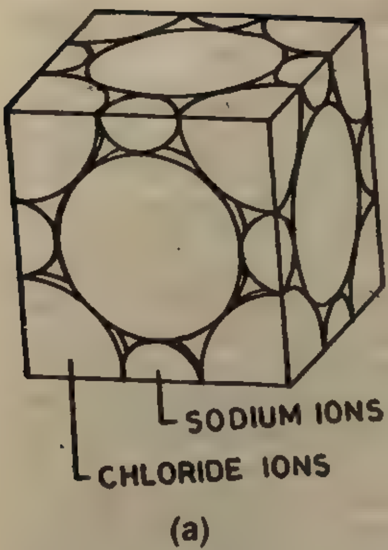


Fig. 2 4 (a)

chloride and sodium ions in the unit cell of NaCl, it has been seen that their ratio is one-to-one. In doing this, it is seen that ions at the corners, along the edges, and in the face-centres are shared with one or more other unit cells.

An ion at the corner of the unit cell is shared with seven others. Figure 2.4 (*a*) shows that only one-eighth of such an ion is in a given unit cell. An ion along an edge, which is shared among four unit cells, has only one-fourth of itself in a given unit cell. An ion in the centre of a face contributes half to a given unit cell, because it is shared between two of them. In addition to these, there is one Na^+ ion that cannot be seen in Fig 2.4 (*a*). It is present in the centre of the unit cell, as shown in Fig. 2.4 (*b*).

For counting the chloride ions, we observe that they are at the eight corners and in the centres of the six faces.

$$8 \text{ corners} \times \tfrac{1}{8}Cl^- \text{ per corner} = 1Cl^-$$
$$6 \text{ faces} \times \tfrac{1}{2}Cl^- \text{ per face} = 3Cl^-$$
$$\text{Total} \quad \overline{4Cl^-}$$

Thus, four chloride ions are contained within the unit cell. For counting the sodium ions, we can see one ion along each of the 12 edges of the cube; each ion contributes one quarter to the unit cell. Apart from this there is one in the centre that is entirely within the unit cell.

$$12 \text{ edges} \times \tfrac{1}{4}Na^+ \text{ per edge} = 3Na^+$$
$$1Na^+ \text{ in centre} = 1Na^+$$
$$\text{Total} \quad \overline{4Na^+}$$

Thus, the number of sodium ions in the unit cell is also four. This means, therefore, that the Na^+ and Cl^- ions are in a one-to-one ratio, which is necessary for the crystal to be electrically neutral.

Any solid/compound that crystallizes with the rock salt structure must have a one-to-one anion/cation ratio. Sodium chloride and the other alkali halides have formulae that satisfy this condition, and many of them acquire this lattice. Calcium oxide also assumes the NaCl lattice.

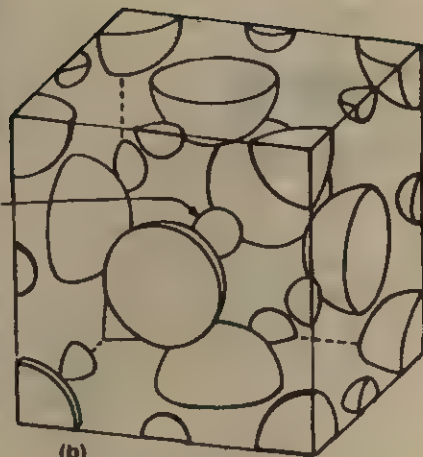


Fig. 2.4 (b). Exploded view of the NaCl unit showing the Na^+ ion in the centre.

Crystals of $CaCl_2$ and Al_2O_3 do not assume the rock salt lattice because their anion/cation ratios do not permit it. Thus, it can be inferred that the formula of a substance places restrictions on the nature of crystal lattice/structure it can and cannot assum e

Caesium Chloride Structure

The caesium ion is sufficiently large to allow eight Cl^- ions to surround it without their touching each other. Thus, the coordination number of the Cs^+ ion is 8 in the CsCl lattice (simple cubic), and the structure possesses 8 : 8 co-ordination. The eight neighbouring Cl^- ions which surround each Cs^+ ion are arranged at the corners of a simple cube, as also are the eight Cs^+ ions which surround each Cl^-. The structure, therefore, consists of a simple cubic arrangement of Cl^- ions which interpenetrates a similar arrangement of Cs^+ ions. Two cubes of each arrangement are shown in Fig. 2.5.

The CsCl type structure is adopted only be compounds in which the cation is large enough to allow eight coordination, *e g.*, CsCl, CsBr, TiCl.

In these structures, both cation and anion thus occupy a cubic hole.

Caesium chloride on heating to 760 K transforms to the NaCl structure with 6 : 6 coordination.

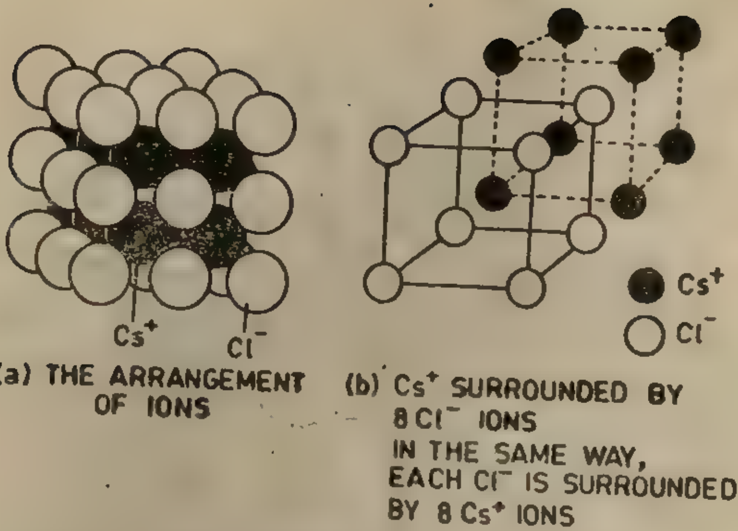


Fig. 2.5. Caesium chloride structure : (a) the arrangement of ions, and (b) two unit cells.

Zinc Blende Structure

The sulphide ions in the zinc sulphide (or zinc blende) lattice form a face centred cubic arrangement [Fig. 2.6 (*a*)]. Each Zn^{2+} ion is

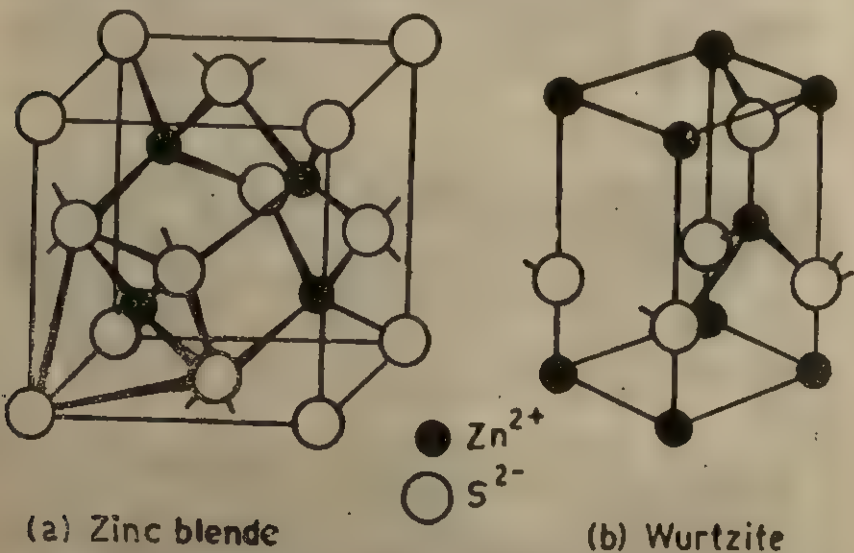


Fig. 2.6. Two crystal lattices of zinc sulphide : Zinc blende and Wurtzite. (a) Zinc blende structure, and (b) Wurtzite structure.

surrounded tetrahedrally by four sulphide ions and, in turn, each S^{2-} ion is surrounded by four Zn^{2+} ions. So each ion has a coordination number of four and the zinc blende structure to possess 4 : 4 coordination. Thus, each ion occupies tetrahedral sites. The lattice of zinc blende resembles the diamond structure with sulphide ions occupying the face centred cubic lattice and zinc ions at four of the eight interior tetrahedral positions.

Zinc sulphide also crystallizes as wurtzite. The wurtzite lattice is hexagonal, with Zn^{2+} ions lying between the planes of a **hcp**-like lattice of S^{2-} ions [Fig. 2.6 (*b*)]. Each ion is surrounded by a tetrahedron of the oppositely charged ions. The difference between the two structures (zinc blende and wurtzite) is in the orientation of these tetrahedra.

Fluorite Structure

The relative sizes of the Ca^{2+} and F^- ions are such that in fluorite (CaF_2), each Ca^{2+} ion has eight F^- ions as nearest neighbours [Fig. 2.7(*a*)]. From the stoichiometry, it follows that each F^- ion is surrounded by a tetrahedron of Ca^{2+} ions, and the coordination of fluorite is thus 8 : 4.

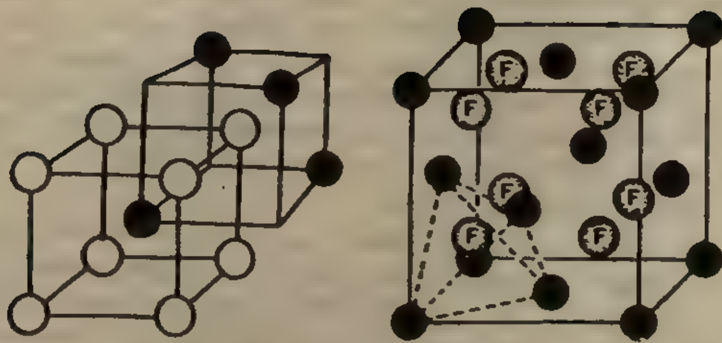
The fluoride ions are arranged so that they are at the corners of simple cubes as seen with CsCl. In CaF_2, only half number of the cubes are filled as warranted by CaF_2. The distribution is regular.

The structure of fluorite is also based upon the zinc blende structure. The calcium ions are arranged in the face centred cubic system and all tetrahedral sites are occupied by fluoride ions. [Fig. 2.7 (*b*)].

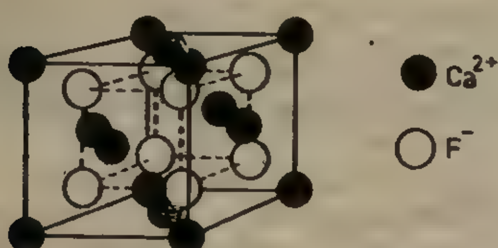
Several ionic compounds of formula AB_2 crystallize with the fluoride structure, *e.g.*, SrF_2, CdF_2 and ThO_2. This structural lattice is also seen in certain compounds with formula A_2B, for example Cs_2O and Na_2O ; in these the positions of cation and anion are interchanged and the lattice is said to have the antifluorite structure. In Na_2O, each oxide ion is coordinated by eight Na^+ ions and each Na^+ ion by four oxide ions.

2.3. CLOSE PACKED STRUCTURES

We have already studied in Class XI that when identical, spherical units are packed together, so that they are just in contact,



(a)



(b)

Fig. 2.7. Fluorite structure : (a) based upon the CsCl structure, and (b) based upon the zinc blende structure.

each sphere is surrounded by 12 others (six in the same layer, three in the layer above and three in the layer below). If the spheres are in contact, there is only 26 per cent interstitial free space in these structures. There is no way of packing spheres to fill the space completely without leaving gaps between them. Two arrangements are possible that represent this maximum efficiency of packing. These lattices, called face centred cubic close packed (**fcc**) and hexagonal close packed (**hcp**) are shown in Fig. 2.8. There are many elements and compounds whose atomic arrangements in solid state can be visualised in terms of close packing of identical spherical units. As already seen these closed packed arrangements involve two types of interstitial holes (or voids)—tetrahedral and octahedral [(Fig. 2·9 *a*), (*b*)].

Close packed structures such as NaCl and CaF_2 also contain these two sorts of 'holes' lying between the close packed planes [Fig. 2·9 (*c*), (*d*)].

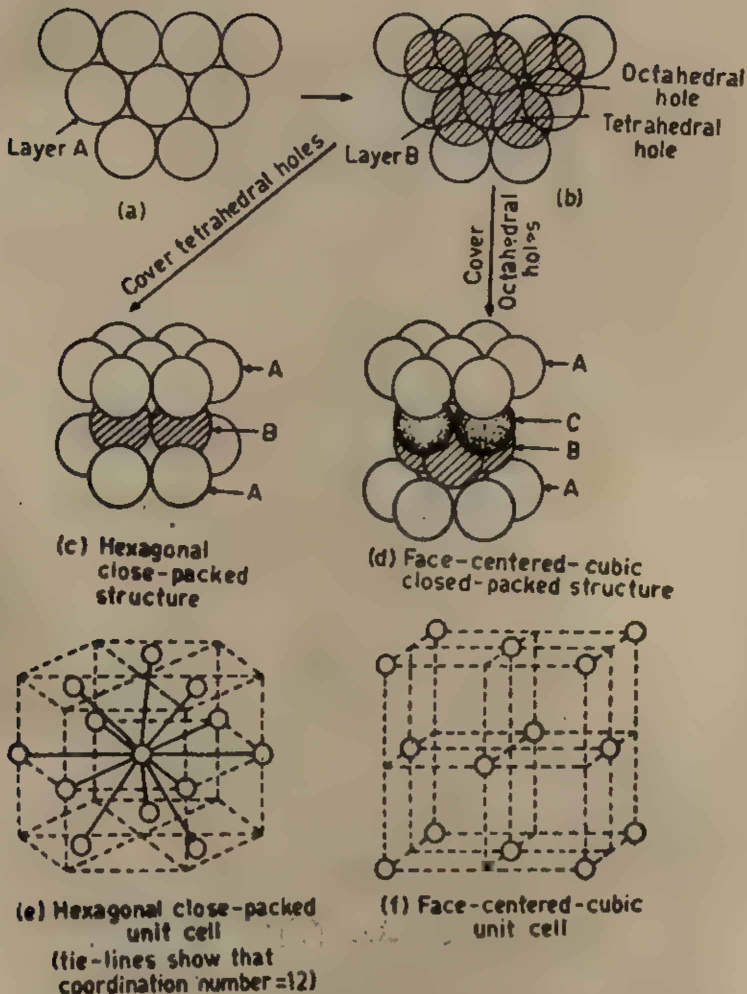


Fig. 2.8. The packing of spheres in the hexagonal close packed (hcp) and the face centred cubic (fcc) close packed structures.

In NaCl, Na^+ ions occupy the octahedral holes in a face centred cubic lattice of Cl^- ions, and the fluoride ions in CaF_2 occupy the tetrahedral holes in a face centred cubic calcium ion lattice.

The radii of the voids in the close packed structures are related to the sizes of the units present in the lattice. The type of structures assumed depends on the radius ratio $\frac{r_c}{r_a}$, where r_c and r_a are the

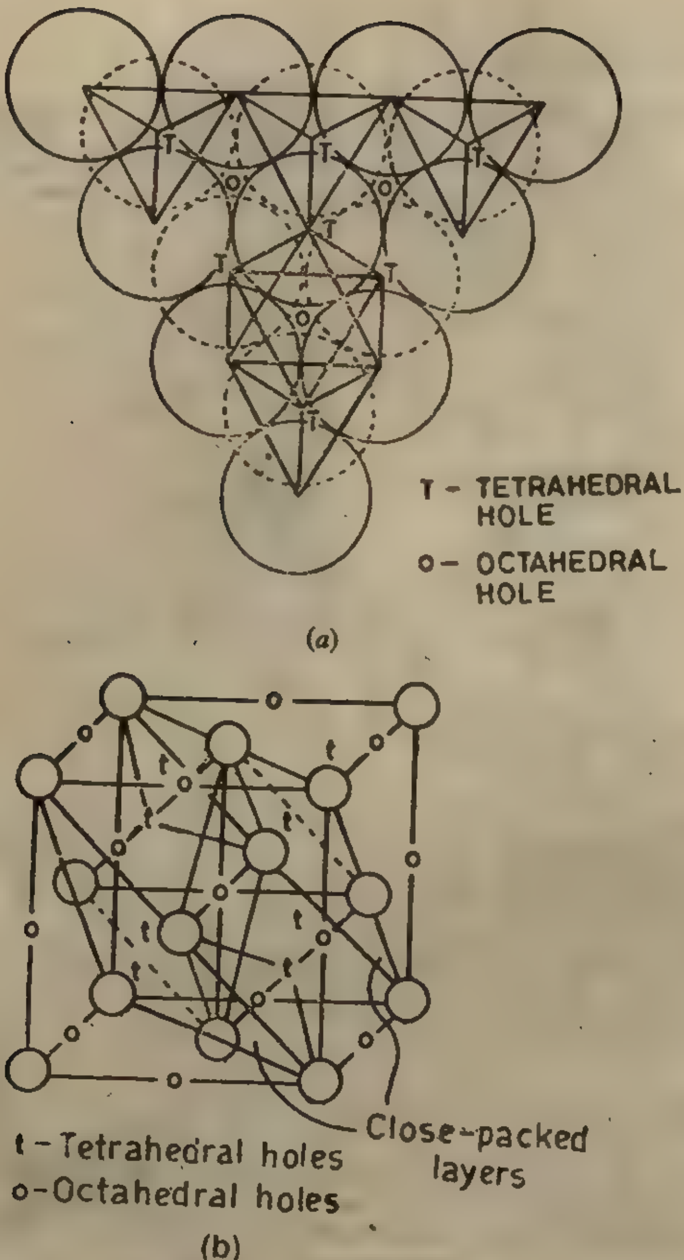


Fig. 2.9. Formation of octa-hedral and tetra-hedral holes in a close packed arrangement of spheres.

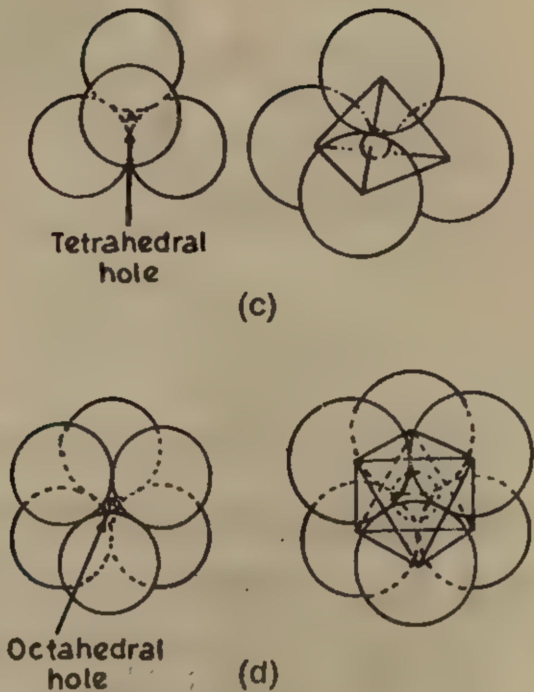


Fig. 2.9. Representation of octahedral and tetrahedral holes in a close packed arrangement of spheres.

radii of the cation and anion. Because of the radius ratio effect and the repulsion of like charges, the limiting coordination numbers commonly encountered in ionic crystals are 8 (body centred cubic lattice, CsCl), 6 (octahedral arrangement, NaCl) and 4 (tetrahedral arrangement ZnS). Figure 2.10 shows the structure of a crystal with a coordination number of 6 in which the anions are just in contact with other anions and with a cation. The Pythagorean theorem allows us to calculate the minimum value of the radius ratio such that the cation can touch one of the anions. Accordingly :

$$2r_a^2+2r_a^2=(2r_a+2r_c)^2$$

which can be solved to yield $\frac{r_c}{r_a}=0{\cdot}414$ for the limiting (minimum) radius ratio for octahedral environment.

If the radius ratio is less than 0·414 (possible with a smaller cation and a bigger anion), a binary compound A^+B^- must assume a structure with coordination number less than 6. A similar calculation shows that if the radius ratio is greater than 0·732, the structure

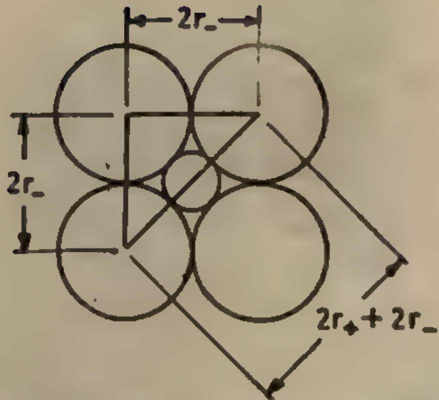


Fig. 2.10. A plane through the octahedral arrangement.

assumed will have a coordination number of 8. Table 2.1 gives the radius ratios for various geometrical environments.

TABLE 2.1. Radius ratios for various geometrical environments.

Radius ratio r_c/r_a	*Coordination number of cation*	*Cation environment (anion arrangement)*	*Example*
0·25—0·41	4	Tetrahedral	ZnS, BeO, CuCl, AgI
0·41—0·73	4	Planar	
0·41—0·73	6	Octahedral	Group 2 oxides (except BeO) Alkali metal halides except caesium halides
0·73—1·00	8	Cubic (hexahedral)	CsCl, CsBr, CsI CaF_2, SrF_2, ClO_2
≳1·00	12	Cubo-octahedral or diseptahedral	

From the description of close packed structures, we are in a position to arrive at some conclusions regarding the structures of some simple ionic compounds. For example, for a ionic solid of the type AB, if the B ions are in a *ccp* arrangement, then the A ions of the opposite charge can occupy all the octahedral voids or one-half of the tetrahedral voids. For an ionic compound of the type A_2B, all the tetrahedral sites will be occupied by A ions. Descriptions of certain typical ionic solids are given in Table 2.2.

TABLE 2.2 Description of ionic solids

Compound	*Ions forming the close packed structure*	*Ions in voids*	*Coordination number*	*Other examples*
NaCl	Cl^- forms ccp structure	Na^+ in all octahedral voids	6 : 6	Halides of Li, Na and K; AgCl, AgBr, CaO,
MgO	O^{2-} forms ccp structure	Mg^{2+} in all octahedral voids	6 : 6	BaO, SrO
ZnS	S^{2-} forms ccp structure	Zn^{2+} in alternate tetrahedral voids	4 : 4	CuCl, CuBr, CuI, BeS
CaF_2	Ca^{2+} forms ccp structure	F^- in all tetrahedral voids	8 : 4	SrF_2
Na_2O	O^{2-} forms ccp structure	Na^+ in all tetrahedral voids	4 : 8	Li_2O, K_2S, Rb_2S

Exercise 2.1. *Compute the free space in a face centred cubic unit cell.*

Solution. Each unit cell in *fcc* consists of eight corner atoms and six face centred atoms. But each corner of a unit cell is also the corner of seven other unit cells. So only $\frac{1}{8}$ of each corner atom belongs to a given unit cell. Similarly, each of the six face centred atoms is shared between two adjacent unit cells, so only $\frac{1}{2}$ of each of these belongs to a given unit cell.

Since there are eight corner atoms and six face centred atoms in a *fcc* unit cell, it contains a total of

$$8\times\tfrac{1}{8}=1 \text{ corner atom}$$
$$6\times\tfrac{1}{2}=3 \text{ face centred atoms}$$
$$\overline{\qquad\qquad}$$
$$4 \text{ atoms, total}$$

Since the volume of each spherical atom is $\left(\frac{4}{3}\right)\pi r^3$, the total volume occupied by the four sphere is

$$4\left(\frac{4}{3}\right)\pi r^3=\frac{16}{3}\pi r^3$$

where r is the atomic radius (or spherical atomic radius). A corner sphere touches a face centred atomic sphere so the distance beween their centres is $2r$, and the length of the face diagonal is $4r$. From this we can find the edge length using the Pythagorean theorem

$$(4r)^2=l^2+l^2$$

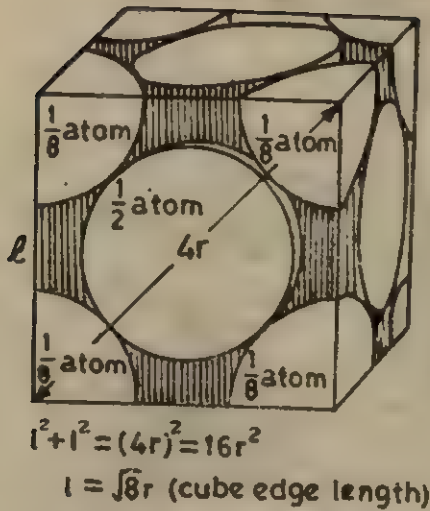


Fig. 2.11. Three dimensional view showing four atoms in case of fcc structure.

where l is the edge length of the unit cell. Solving for l we get,

$$2l^2=16r^2$$
$$l^2=8r^2$$
$$l=r\sqrt{8}$$

The volume of the cube is, therefore

$$V=l^3=(r\sqrt{8})^3=8\sqrt{8}r^3$$

The percentage of filled space is, therefore,

$$\frac{\text{Volume of spheres}}{\text{Volume of cube}}\times 100=\frac{\left(\frac{16}{3}\right)\pi r^3}{8\sqrt{8}r^3}\times 100$$
$$=\frac{2\pi}{3\sqrt{8}}\times 100=74\%$$

The remaining 26% of the volume is free space.

Exercise 2.2. *A face centred cubic element (atomic mass 60) has a cell edge of 400* pm. *Calculate its density.*

Solution. Cell edge 400 pm

Volume of the unit cell, $V^3=l^3$

$$=(400)^3\ (\text{pm})^3$$
$$=400^3\ 10^{-30}\ \text{cm}^3$$

$$\text{Density of the unit cell}=\frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

Mass of the unit cell = Number of the atoms in the unit cell × Mass of each atom

$= Z \times m$

Mass of each atom, $m = \dfrac{\text{Atomic mass}}{\text{Avogadro's number}}$

$= \dfrac{60}{6.02 \times 10^{23}}$

Density of the unit cell $= \dfrac{60 \times 4}{400^3 \times 10^{-30} \times 6.02 \times 10^{23}}$

(A unit cell contains 4 atoms)

$= \dfrac{60 \times 4}{64 \times 6.02 \times 10^{-1}}$

$= 6.23 \times \text{g cm}^{-3}$.

Exercise 2.3. *How many atoms are there per unit cell in (a) simple cubic arrangement of atoms (b) body centred cubic arrangement, of atoms, and (c) face centred cubic arrangement of atoms?*

Solution. In a three dimensional cubic lattice

(*a*) each corner atom is shared by 8 cubes *i.e.*, its one-eighth part belong to each cube (Fig. 2.12 *a*).

(*b*) the centred atom in a body centred cube is not shared by any other cube (Fig. 2.12 *b*).

(*c*) Already explained in Exercise 2.1.

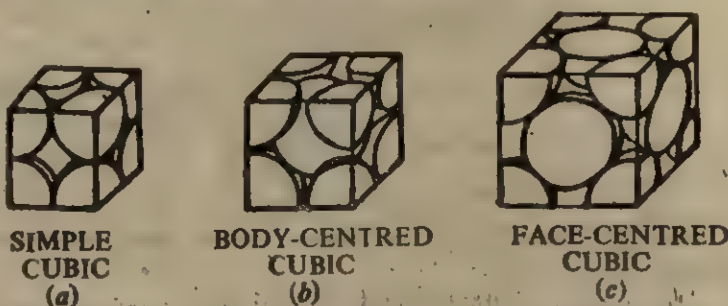


Fig. 2.12. Three dimensional view showing atoms per unit cell: (a) one atom per unit cell in case of simple cubic arrangement, (b) two atoms per unit cell in a body centred cubic structure, and (c) Four atoms per unit cell.

The number of atoms in,

(*a*) simple cubic arrangement is $\frac{1}{8} \times 8 = 1$ atom.

(*b*) body centred cubic arrangement is $(\frac{1}{8} \times 8) + 1 = 2$ atoms.

(*c*) face centred cubic arrangement is four atoms.

Exercise 2.4. *The compound CuCl has the ZnS structure. Its density is 3.4* g cm^{-3}. *What is the length of the edge of the unit cell.*

Solution. ZnS assumes *fcc* arrangement. Therefore, the number of atoms per unit cell is four.

$$\text{Density of the unit cell} = \frac{\text{Number of atoms in the unit cell} \times \text{mass of each atom}}{\text{Volume of unit cell} \times \text{Avogadro's number}}$$

$$3.4 \text{ g cm}^{-3} = \frac{4 \times (6.5 + 35.5) \text{ g}}{a^3 \times 6.02 \times 10^{23}}$$

$$a^3 = \frac{99 \times 4}{3.4 \text{ cm}^{-3} \times 6.02 \times 10^{23}}$$

$$a^3 = 19.34 \times 10^{-23} \text{ cm}^3$$

$$a = 5.784 \times 10^{-10} \text{ cm} = 578 \text{ pm.}$$

Exercise 2.5. *Calculate the value of the Avogadro's number from the following data :*

Density of silver $= 10.6$ g cm^{-3}

Atomic mass of silver $= 107.9$ g mol^{-1}

Edge of fcc system of Ag $= 0{\cdot}408$ nm.

Solution. The unit cell has a volume of $(0.408 \times 10^{-9} \text{m})^3 = 6.79 \times 10^{-29}$ m^3 per unit cell and contains four atoms.

The volume of 1 mole of silver is

$$= 107.9 \text{ g mol}^{-1} / 10.6 \text{ g cm}^{-3}$$

$$107.9 \text{ g mol}^{-1} \times \frac{\text{cm}^3}{10.6 \text{ g}}$$

$$107{\cdot}9 \text{ g mol}^{-1} \times \frac{(1 \times 10^{-2} \text{ m})^3}{10.6 \text{ g}} = 1.02 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

The number of unit cells per mole is

$$1.02 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \left(\frac{1 \text{ unit cell}}{6.79 \times 10^{-9} \text{ m}^3} \right)$$

$= 1.50 \times 10^{-23}$ unit cells per mole and the number of atoms per mole is

$$\frac{4 \text{ atoms}}{\text{unit cell}} \left(\frac{1.50 \times 10^{23} \text{ unit cells}}{\text{mole}} \right) = 6.0 \times 10^{23} \text{ atoms mol}^{-1}$$

2.4. IONIC RADII

In ionic crystals the ions may be regarded as in contact with one another and so the measured interatomic distance corresponds with the sum of the radii of the cation and anion. As in the case of atomic radii, it is useful to have the knowledge of the relative sizes of ions and several attempts have been made to arrive at a suitable set of ionic radii. We need to know the radii of ions to calculate the radius ratios which have been useful to understand the structures of ionic crystals.

The distances between the centres of adjacent ions in an ionic crystal can be measured by X-ray diffraction with considerable accuracy. X-ray diffraction pattern of ionic crystals provide dimensions of unit cells. From the dimensions of unit cells one can calculate the radii of ions.

Pauling, from the experimental values of interionic distances in a number of crystals—namely NaF, KCl, RbBr, CsI, deduced a set of ionic radii which closely reproduce the interionic distances in many other compounds. A set of values for radii of ions based on the analysis of a very large number of crystal structures is given in Table 2.3. Such a set of ionic radii assumes that an ion always has exactly the same size, *i.e.*, each ion behaves as a hard sphere.

TABLE 2.3. Ionic radii/pm in crystals

Li^+	60	Be^{2+}	31	Al^{3+}	50	Si^{4+}	41	O^{2-}	140
Na^+	95	Ca^{2+}	65	Tl^{3+}	95	Ti^{4+}	68	S^{2-}	184
K^+	133	Sr^{2+}	99			Sn^{4+}	71		
Rb^+	148	Ba^{2+}	113			Pb^{4+}	84	F^-	136
Cs^+	169	Zn^{2+}	74					Cl^-	181
Cu^+	96	Cd^{2+}	97					Br^-	195
Ag^+	126							I^-	216

There is a good agreement between the observed values of interionic distances and those calculated from a set of ionic radii (Table 2.4).

TABLE 2.4. Comparison of the observed interionic distance with the calculated value in alkali halide crystals

Crystal	*Observed distance*/pm	*Calculate distance*/pm	*Crystal*	*Observed distance*/pm	*Calculate distance*/pm
LiF	201	196	LiCl	257	241
NaF	231	231	NaCl	281	276
KF	266	269	KCl	314	314
RbF	282	284	RbCl	329	329
CsF	300	305	CsCl	347	350

The ionic radii show a number of interesting trends :

(*i*) In moving from left to right across a period, a sequence of isoelectronic cations and anions shows a marked decrease in radius, for example,

from : $Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$

from : N^{3-} (171 pm) $>$ O^{2-}(140 pm) $>$ F^-(136 pm)

This is because of the fact that the increasing nuclear charge with atomic number acts on the same number of electrons, and hence , the radius of the ion decreases.

(*ii*) In moving down a group of elements (other than transitional elements), the ionic radius increases both for cations and anions. In going from one element to next of higher atomic number, an extra shell of electrons is interposed between the nucleus and the outermost valence electrons. As a result, the nuclear charge also increases, the effect of which is more than offset by the additional screening effect of the extra electrons.

2.5. SILICATES

Silicate minerals and complex aluminosilicate clays are present in abundance in the earth's crust. Their weathered products, *e.g.*, soils, clays, and sand consist almost entirely of silicates and silica The silicates are usually giant molecules rather like silica, but which contain many other metallic elements in addition to the silicon and oxygen. Quartz, mica, asbestos, felspars, and zeolites are all silicate minerals. The glass, ceramic and cement industries are based on silicate chemistry.

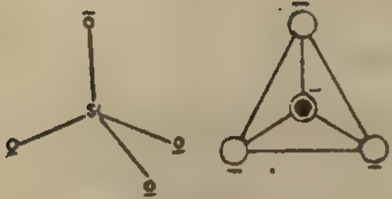
The vast majority of silicates are highly insoluble (only alkali metal silicates are water soluble). A common feature to all these complex silicate anions is SiO_4^{4-} tetrahedra, the basic structural units.

These tetrahedra can exist either as discrete structural entities or can combine by corner sharing of oxygen atoms into large units.

The resulting oxide ion lattice is frequently close-packed or approximately so. Since these silicate rocks are electrically neutra. they must also contain a sufficient number of cations such as Na^+ K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} to balance all the negative charges carried by the oxygen atoms. These cations, according to their size, occupy tetrahedral, octahedral or other sites present in the crystal lattice of silicates. The SiO_4 units can build up into chains, multiple chains (or ribbons), rings, sheets and three-dimensional networks summarized in Table 2.5 and Fig 2.13.

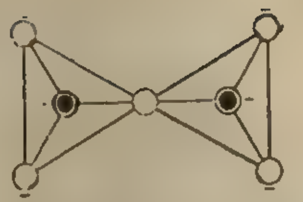
TABLE 2·5. Structural arrangement of SiO_4 units

	Structural arrangement	*Anion unit*	*Example*
(*i*)	**Discrete anions :**	$(SiO_4)^{4-}$	**Orthosilicates :** Zircon, $ZrSiO_4$; Phenacite, Be_2SiO_4 ; Forsterite, Mg_2SiO_4
	Two tetrahedra sharing one oxygen	$(Si_2O_7)^{6-}$	**Pyrosilicates :** (examples of island structures) Thortveitite, $Sc_2Si_2O_7$ Akemanite, $Ca_2MgSi_2O_7$
	Closed rings of tetrahedra, each sharing two oxygens	$(Si_3O_9)^{6-}$	Cyclic silicates : Benitoite, $BaTiSi_3O_9$; Wollastonite $Ca_3(Si_3O_9)$
		$(Si_6O_{18})^{12-}$	Emerald (mineral beryl) $Be_3Al_2Si_6O_{18}$
(*ii*)	**Extended anions** Continuous single chains of tetrahedra, each sharing two oxygens	$(SiO_3)_n^{2n-}$	**Pyroxenes :** like Diopside, $CaMg(SiO_3)_2$; Spodumene, $LiAl(SiO_3)_2$; Enstatite, $(MgSiO_3)_2$
	Continuous double chains of tetrahedra sharing alternately two and three oxygens	$(Si_4O_{11})_n^{6n-}$	**Amphiboles :** like Tremolite, $(OH)_2Ca_2Mg_5(Si_4O_{11})_2$ Anthophyllite, $(OH)_2Mg_7(Si_4O_{11})_2$ Asbestos have these double chains but the structures are more complex
	Continuous sheets of tetrahedra, each sharing three oxygens with other Si atoms to give large sheets	$(Si_2O_5)_n^{2n-}$	**Talc,** $Mg_3(Si_2O_5)_2(OH)_2$; **Kaolinite,** $Al_2(Si_2O_5)(OH)_4$ Micas and clays belong to this class of silicates
(*iii*)	**Three dimensional networks**		There are the various forms of silica (quartz, tridymite and cristobalite)
	Continuous framework of tetrahedra, each sharing all four oxygens	SiO_2	**Cristobalite,** SiO_2 **Quartz,** SiO_2 Feldspars e.g., Albite, $NaAlSi_3O_8$; [*e.g.*, Orthoclase $KAlO_2(SiO_2)_3$] and the open framework zeolite [*e.g.*, analcite; $AlSi_2O_6.H_2O$] also assume this arrangement.



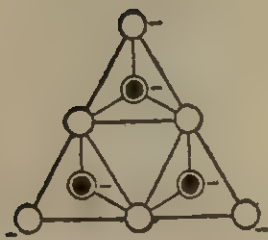
SiO_4^{4-} ion (O = o, • = Si)

$(SiO_4)^{4-}$



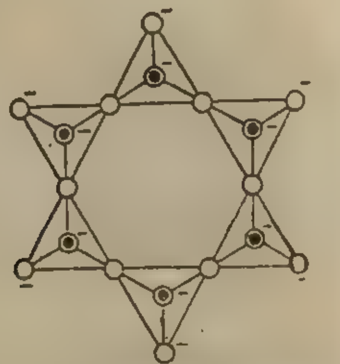
$Si_2O_7^{6-}$ ion (O = o, • = Si)

$(Si_2O_7)^{6-}$



cyclic silicate (O = o, • = Si)

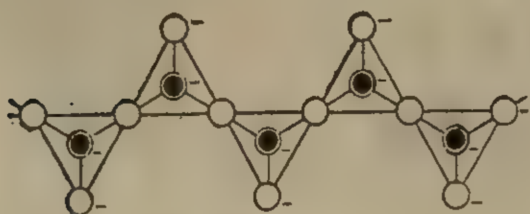
$(Si_3O_9)^{6-}$



O OXYGEN • SILICON

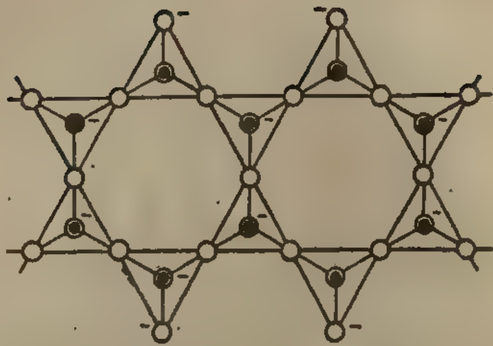
$(Si_6O_{18})^{12-}$

Fig. 2.13 (a) Structures of discrete anions involving SiO_4 tetrahedra ● *=silicon ;* O*=oxygen*

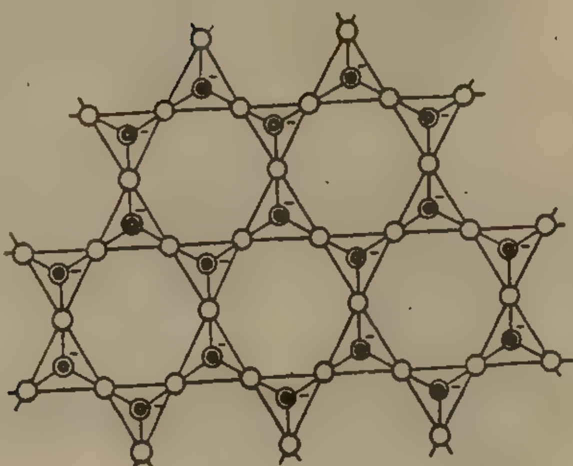


Chain silicate $(SiO_3)_n^{2n-}$ (O = o, • = Si)

$(SiO_3)_n^{2n-}$



$[(Si_4O_{11})_n]^{6n-}$



$[(Si_2O_5)_n]^{2n-}$

Fig. 2.13 (b) Structures of extended anions : chains and sheets of silicate tetrahedra. ● *=silicon ;* O*=oxygen*

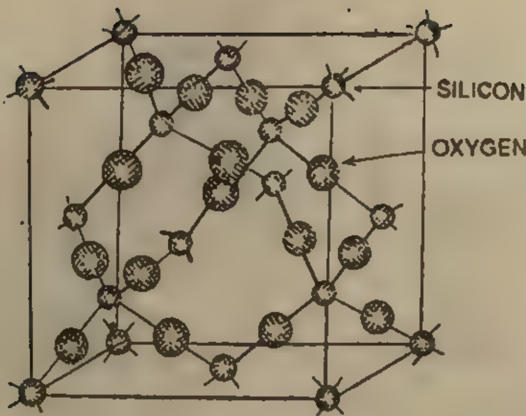


Fig. 2.13 (c) Structures of three dimensional networks of SiO_4 tetrahedra

From Table 2.5 it is evident that the molecular formulae of some silicates contain metals other than silicon, *e.g.*, Al, Ca, Mg, *etc*. This could be possible by the replacement of Si^{4+} by Al^{3+} ions to give aluminosilicates. As a result, the network will carry an overall negative charge which is counterbalanced by the incorporation of cation such as Na^+ and Ca^{2+} into the cavities in the structure. In this way materials such as feldspars [*e g.*, orthoclase, K AlO_2 $(SiO_2)_3$] and the open frame work zeolite structures are produced. Zeolites are three-dimensional silicates, *e.g.*, analcite (empirical formula Na^+ $[Al\ Si_2O_6]^-H_2O$. Zeolities can be used as ion exchangers, whose operation depends on replacing one kind of cation with another in these cavities. They are used in the treatment of hard water. Anhydrous zeolites are useful for drying organic solvents and adsorbing impurities from gases such as N_2 and H_2. Because of this, they are called molecular sieves ; the small H_2O molecules can get into the cavities but larger molecules cannot. The affective separation of straight chain alkanes from the branched chain or aromatic substances has been achieved by using zeolites.

Clays are aluminosilicates with the infinite sheet structures, and usually colloidal in nature. Kaolinite is a clay widely used in making pottery. Asbestos is a fibrous silicate with either the chain or sheet structure, *e.g.*, crysolite, 3MgO, $2SiO_2$, $2H_2O$ has the sheet structure.

Micas have infinite sheet structures. Muscovite $K_2\ Al_4$ $[Si_6\ Al_2O_{20}]\ (OH)_4$ is an example of mica.

Glass and cement are the two well-known synthetic silicates.

2.6. IMPERFECTION IN SOLIDS

A crystal which contains all its constituent particles arranged at its lattice points without any defect is defined as an ideal crystal. But

it is seldom that we come across a perfect or an ideal crystal. Many crystalline minerals valued as jewels, are nearly perfect crystals, *i.e.*, the defects are very few. It is nearly impossible to achieve a completely regular crystal. Even in a chemically pure crystalline substance a variety of errors occur during the growth of a lattice.

Slow growth of a crystal minimizes the chance of crystal imperfections, and a rapidly formed crystal incorporates the most errors. As the crystal 'grows', an extra layer of particles may form part way through the crystal, resulting in a dislocation of the particles at the crystal face and a visible irregularity.

These give rise to **physical, intrinsic** or **native defects.** Other types of defects may include substitution of the atoms in some positions of the lattice by atoms of another substance, or accommodating atom of another substance into the interstices. The defects may be of such a nature that the regularity of the arrangement of constituent particles might be destroyed to the extent the impurities are present in the crystal. These defects may be called as **extrinsic or chemical defects.** Obviously the chemical composition of the crystalline substances possessing chemical defects would change to the extent of impurity level. But the presence of physical defects does not produce any change in the chemical composition of the crystal. We shall be more concerned with discussions of chemical defects. These can cause marked changes in the physical properties of the crystal, like conductivity and diffusion. Sometimes certain chemical properties may also be modified. Some of these defects are discussed in the following sub-sections :

2.6.1 Electronic Imperfections

In an ionic crystal, essentially all electrons are localized, bound to specific atoms (generally more electronegative). Raising the temperatures, frees some electrons which become delocalized. As the temperature goes up, more weakly bound electrons are made available. Such electrons move freely through the crystal and are responsible to conduct electric current. The electron deficient bond obtained by the removal of an electron is referred to as a **'hole' (or vacant orbital)**. Holes also give rise to electrical conductivity, as electrons can move from neighbouring atoms to these holes. These electrons and holes are considered to be electronic imperfections. Electrons and holes are generally designated by the symbols 'e' and 'h' respectively, and their concentrations by n (negative) and p (positive). More about this will be discussed later under electrical properties.

2.6.2 Atomic Imperfections

In atomic imperfections, irregularity recurs in the lattice structures. Irregularities at single atom sites are referred to as **lattice and defects** . Lattice imperfections may extend beyond a point along lines (**line defects**) or surfaces (**plane defects**). Line defects are also called **dislocations.**

1. Dislocations

Dislocation can be of two types : edge and screw dislocations. Edge dislocation (Fig. 2.14) results from the missing of a plane. A

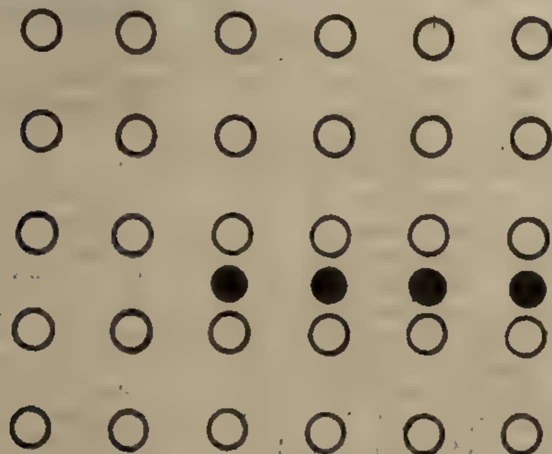
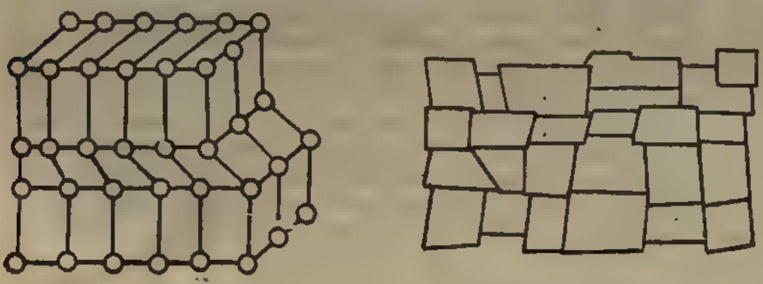


Fig. 2.14. Edge dislocation.

times a layer or plane of particles stops within the crystal rather than continuing all the way through. Fig. 2.14 shows a schematic representation of an edge dislocation, wherein one of the layers has stopped partway through the crystal, creating a dislocation. It is also likely that in a crystal one block is not perfectly set with the next. In such cases there is a strain between one block and the next. Such a strain is called edge dislocation [Fig. 2.15 (*a*)]. Correction of this strain may result in displacement of one block with respect to the next [Fig. 2.15 (*b*)]. Such crystals can be cleaved readily.



(*a*) (*b*)

Fig. 2.15. (a) Edge, and (b) block dislocations.

Screw dislocation is closely connected with crystal growth. It gives rise to a spiral stairway type of face as shown in Fig. 2.16. Dislocations are centres of enhanced chemical reactivity ; corrosion

of metals occurs more rapidly where there is a high surface concentration of dislocations.

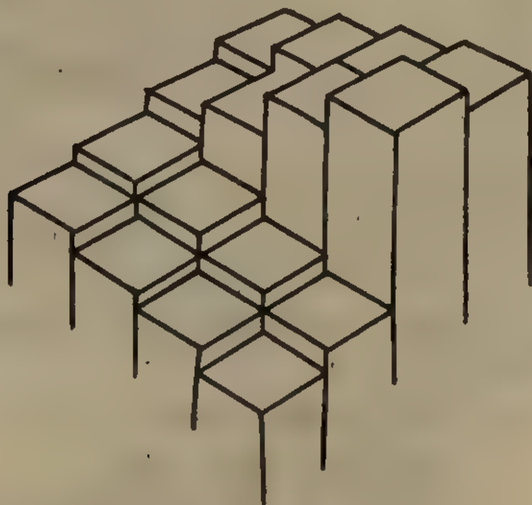
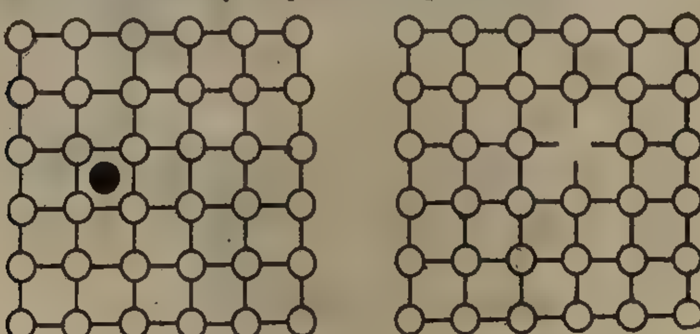


Fig. 2.16. Screw dislocation.

2. Point defects

These include the lattice vacancy and the lattice interstitial (Fig. 2.17). If any of the constituent particles of the crystal is missing from the position it should occupy in a perfect crystal lattice, a lattice vacancy occurs which leads to defect. This particle may be present in a position in the lattice which is not meant for it or even the particle may occupy the interstices in the lattice, or it may be dislocated to a position meant for another atom. All these situations give rise to defects in a crystal, and these types of defects are called **point defects**. The stoichiometric composition of the crystals is not affected by the presence of point defects.



(a) (b)

Fig. 2.17. Point defects: (a) lattice vacancy, and (b) lattice interstitial.

The electrical neutrally is, however, maintained inspite of these defects.

In stoichiometric ionic solids, point defects occur in two common combinations : the **Schottky defect** [Fig. 2.18 (*b*)] is a pair of lattice vacancies of opposite charge and the **Frenkel defect** [Fig. 2.18 (*c*)] is an ion misplaced in an interstitial position plus the vacancy where it ought to be.

In a Schottky defect, the migration of cation and anion from their lattice sites to a surface of a crystal (form a new layer of the normal crystal lattice) takes place, creating a pair of lattice vacancies in the crystal lattice [Fig. 2.18 (*b*)]. In a Frenkel defect, an ion moves from its normal lattice point into the interstices as shown in Fig. 2.18 (*c*). It also leaves a lattice vacancy or void.

Figure 2.18 (*a*) represents the lattice for a perfect crystal. The defects shown have maintained electrical neutrality and do not affect

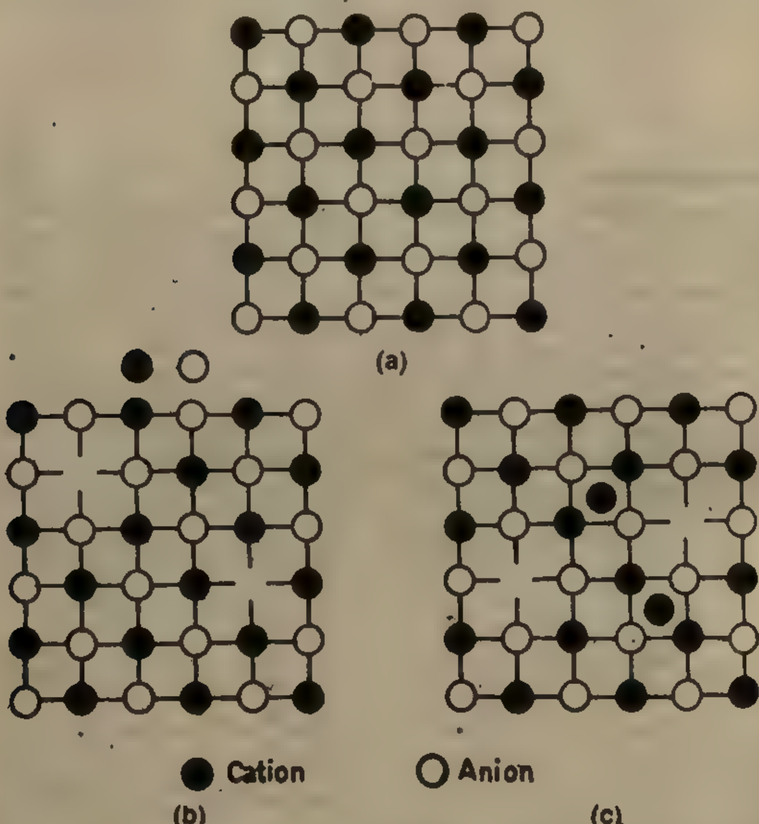
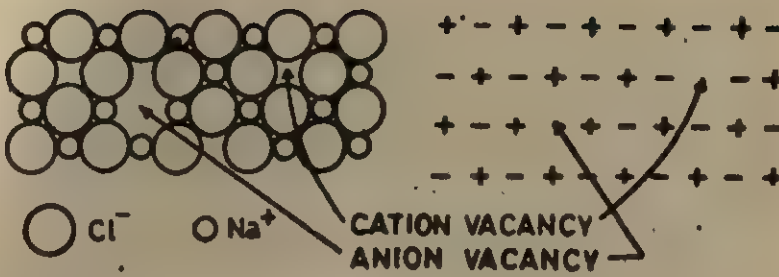
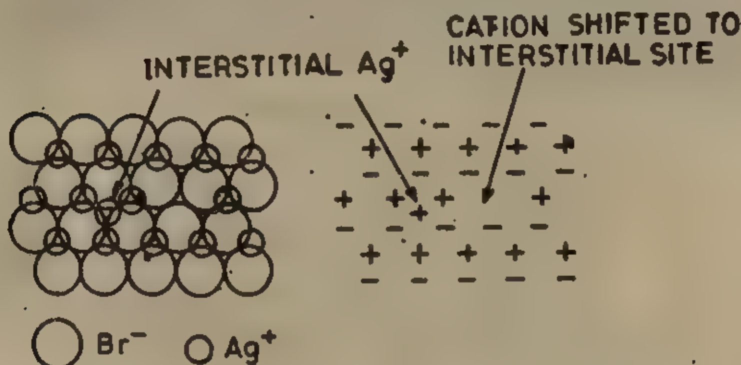


Fig. 2.18. (a) Perfect crystal, (b) Schottky defect, and (c) Frenkel defect.



(d)

Fig. 2.18. (d) Schottky defects in sodium chloride.



(e)

Fig. 2.18. (e) Frenkel defects in silver bromide.

the stoichiometry of an ionic solid. Schottky defect alone decreases the overall density of the crystalline substance.

It is, however, quite obvious that crystals showing Schottky defect would be less dense than the perfect crystal to the extent such imperfections are present. But for the crystal possessing Frenkel defects, there will be no change in density.

Alkali halides suffer from Schottky defects [Fig. 2.18 (*d*)]; Frenkel defects are not found in alkali halids as the ions do not move into the intestitial sites. It is seen in silver halides because of the small size of Ag^+ ion [Fig. 2.18 (*e*)]. In certain solids (*e.g.* AgBr) both Schottky and Frenkel defects occur.

Defects in non-stoichiometric solids

Non-stoichiometric solids are those in which the ratio of positive and negative ions present differs from that indicated by the ideal chemical formula. In compounds such as FeO, FeS, CuO,

TiO, ZrO and Cu_2S, the real composition of constituent ions can vary. Cuprous sulphide, for example, may contain anything between $Cu_{1.96}S$ and Cu_2S. The balance of positive and negative charges is maintained either by having extra electrons or extra positive charges present. This makes the structure irregular, *i.e.*, it contains the defect in addition to Schottky and Frenkel defects. These additional defects arise because either the metal or non-metal atoms are present in excess.

In general, these effects turn out to be of four types :

(*i*) with vacant cation sites

(*ii*) with vacant anion sites

(*iii*) with supernumerary anions occupying interstitial sites

(*iv*) with supernumerary cations occupying interstitial sites

As these effects as well maintain electrical neutrality, some cations in (*i*) and (*iii*) cases carry additional charge to compensate for missing cations; some free electrons in (*ii*) and (*iv*) cases exist to compensate for the missing anions.

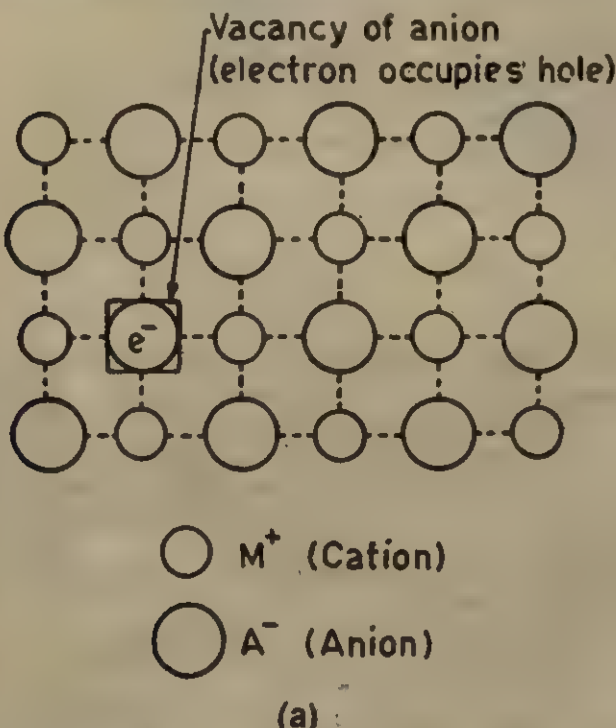


Fig. 2.19. (a) Metal excess defect due to missing anion : a representation.

Metal excess defect

This occurs because of the following :

(*i*) A negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron thereby maintaining the electrical neutrality [Fig. 2.19 (*a*)]. This defeat is rather similar to Schottky defect and is found in crystals which are known to have Schottky defects. For example, when NaCl is treated with sodium vapour, a yellow coloured non-stoichiometric form NaCl is obtained in which there is an excess of sodium ion.

Anion vacancies in alkali metal halides are created when alkali metal halide crystals are heated in an atmosphere of the alkali metal vapour. When the metal atoms form a layer on the surface of the alkali halide crystal, halide ions diffuse into the surface and combine with the metal atoms. The electrons obtained by the ionization of the alkali metal atoms then diffuse within the crystal and occupy a negative ion vacancy. Electrons located in anion vacancies are referred to as F CENTRES [Fig. 2.19 (*b*)] which give rise to interesting properties. Thus, the excess of potassium in KCl makes the crystal appear violet and the excess of lithium in LiCl makes it pink.

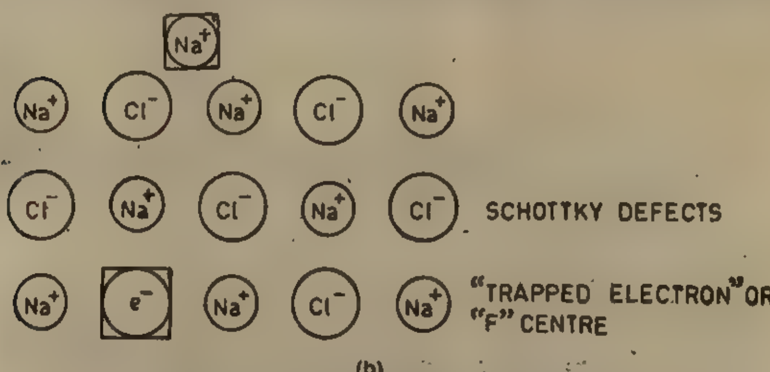


Fig. 2.19. (b) Defects in sodium chloride.

(*ii*) A second way in which metal excess defect occurs, when an extra positive ion occupies an interstitial position in the lattice. An electron which is also present in an interstitial position helps to maintain the electrical neutrality. This is illustrated in Fig. 2.20 (*a*) and (*b*). This defect is like Frenkel defect and is much more common than the first. It is found in crystals which are expected to have Frenkel defects.

Zinc oxide on heating loses oxygen reversibly and acquires yellow colour. The excess metal is accommodated interstitially in the cationic form. The enhanced electrical conductivity of non-stoichiometric ZnO arises from these electrons. Lattice defect for ZnO is shown in Fig. 2.20 (*b*). CdO also suffers from this defect. The ionized electrons are trapped in the neighbourhood.

Crystals with either type of metal excess defects contain free electrons and if these migrate, they conduct electricity. Since there are few defects (hence a few free electrons), the amount of current carried is very small. These crystal thus act as **semi conductors.** The free electrons in such crystals can be excited to higher energy levels giving absorption spectra and as a consequence the compounds get coloured. ZnO is yellow when hot and white when cold.

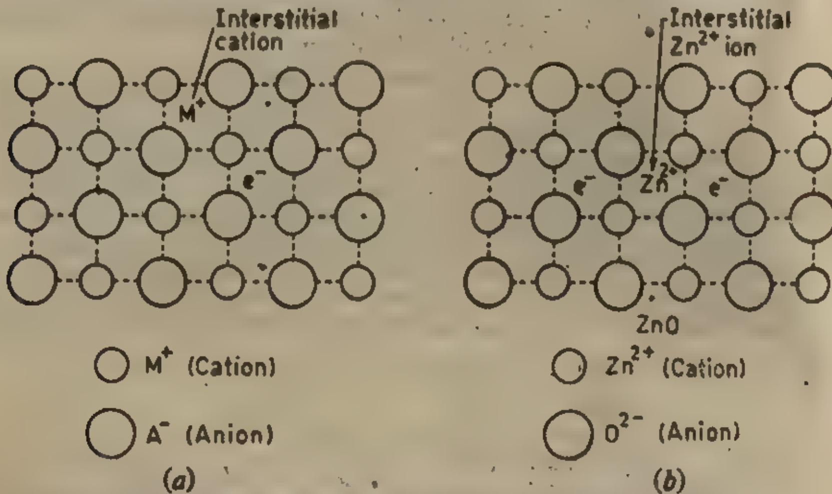


Fig. 2.20. (a) Metal excess defect caused by interstitial cation : (a) a representation. (b) Zinc oxide lattice acquires interstitial metal in the cationic form.

Metal deficiency defect

Some compounds suffer from cationic deficiency caused by missing cation. This deficiency could be accounted for in two ways (*i*) a number of adjacent metal ions exist in a higher oxidation state to compensate for the missing cation [Fig. 2.21 (*a*) and (*b*)]. This is how the electrical neutrality is maintained FeO, FeS and NiO provide examples of this type of defect. Thus, in FeO there are a number of Fe^{3+} ions to compensate for the missing Fe^{2+} ions [Fig. 2 20 (*b*)]. The presence of atoms in a different oxidation state in a defective lattice makes the flow of electrons easy.

(*ii*) An extra negative ion may be present in an interstitial site. The corresponding increase in the negative charge is balanced by the oxidation of an adjacent metal ion (Fig. 2.22). Since anions are usually large, it is difficult to expect them to be present at interstitial sites.

Crystal with metal deficiency defects act as semi-conductors. Such defects can also generate metallic conduction in non-metallic substances.

At times in an ionic crystal, the cations or anions may be replaced by an impurity ion of higher charge and matching size.

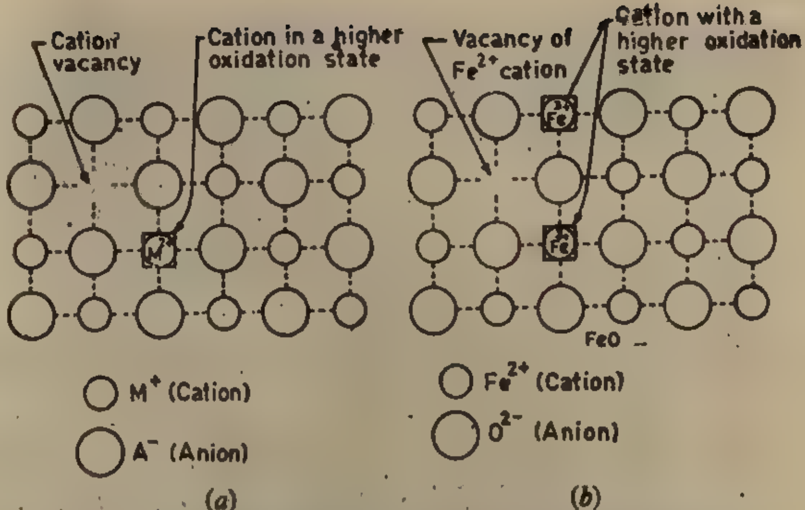


Fig. 2.21. Metal deficiency defect caused by missing cation (a) a representation and (b) presence of defects in FeO.

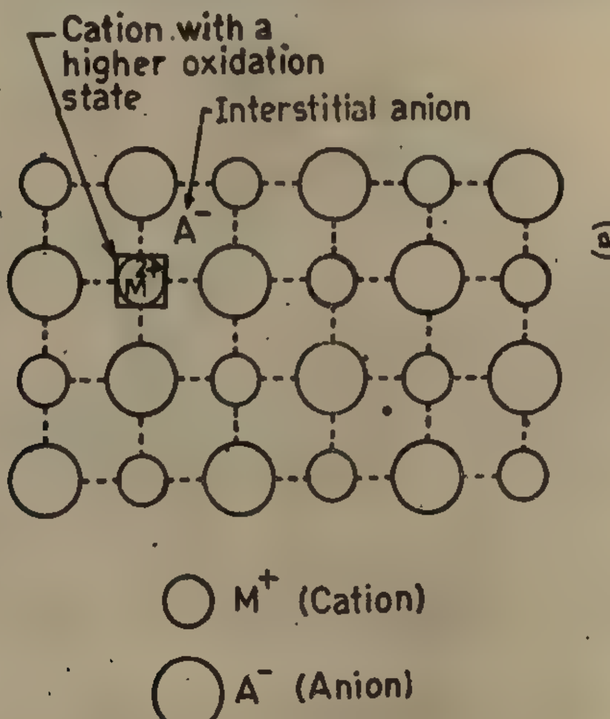


Fig. 2.22. Metal deficiency defects caused by an interstitial anion : a representation.

Such impurity defects are also classed as point defects. Figure 2.23 depicts the defect produced in a crystal of AgCl when Zn^{2+} ion impurity replaces one Ag^+ ion from its lattice position. To fulfil the requirement of electrical neutrality another Ag^+ ion will be missing

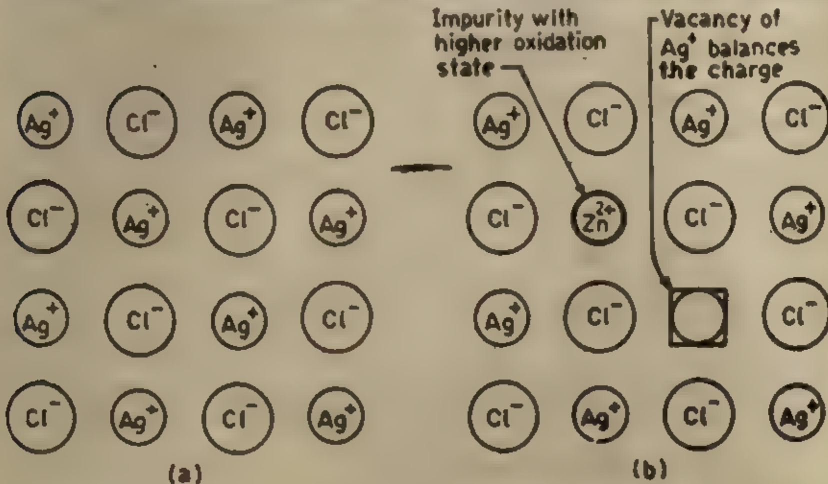


Fig. 2.23. AgCl crystal : (a) in absence of impurity, (b) the presence of impurity of Zn^{2+}. ○ Denotes vacancy.

from its lattice position leaving behind a vacancy. Such a vacancy in due course is filled when a Ag^+ ion moves from a neighbouring lattice position, causing a fresh vacancy, which in turn can be filled in a similar manner, and the recurrence of this phenomenon can be regarded as equivalent to movement of Ag^+ in one direction and the vacancy in the opposite direction. This gives rise to conduction of electricity through the crystal. To increase the conductivity of solids, defects are deliberately introduced by adding such impurities to perfect or near perfect crystals.

Molten sodium chloride mixed with a small amount of $CaCl_2$ on crystallizing results into a lattice which has an occasional Ca^{2+} where an Na^+ ought to be. To maintain the electrical neutrality, for each Ca^{2+} ion present a cation vacancy (a missing Na^+) appears in the crystal (Fig. 2.24). Similarly, ZnS can be prepared with Cl^- ions replacing some of the S^{2-}. For every two Cl^- ions, a cation vacancy is present. The addition of a small amount of impurity to a compound before it crystallizes is called **doping**. Doping often changes the properties of a substance greatly. Sodium chloride doped with $CaCl_2$ has a much higher electrical conductivity than does pure NaCl.

The non-stoichiometric chemical composition of crystalline substances may be attributed to the existence of several of such defect sites as discussed above. The compounds whose crystals are

capable of possessing non-stoichiometric defects may be called non-stoichiometric compounds. These are important because they possess desirable properties of semiconductors. These compounds are also named as **berthollides** named after Claude Louis Berthollet who discovered that chemical composition of such compounds varies continuously within certain limits.

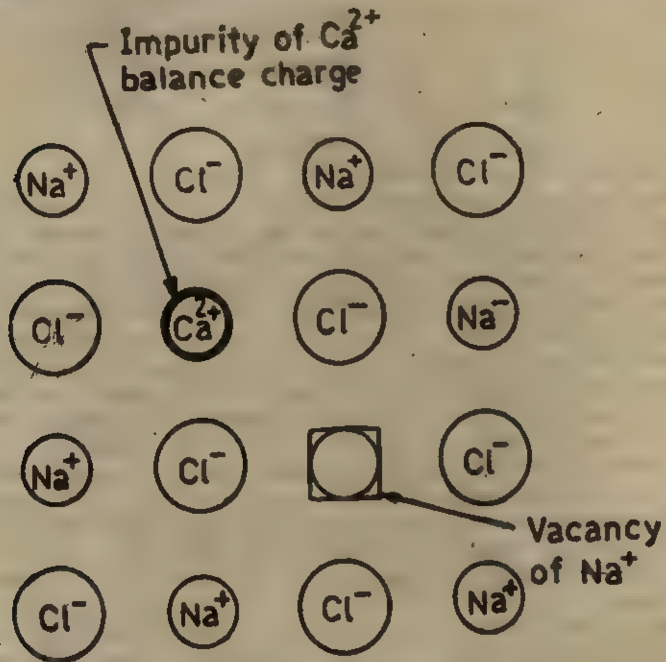


Fig. 2.24. Introduction of cation vacancy in NaCl by substitution of Na^+ by Ca^{2+}

The natural luster or the shining colour of the pyrite minerals can be attributed to this defect. Some samples of naturally occurring pyrites possess so much luster that these are known as **fools gold.** It may be interesting to note that existence of this type of defect in crystals of non-metals where the non-metallic ions of different oxidation states exist side by side, gives rise to very interesting colours to such minerals. Table 2.6 includes certain compounds with possible defects.

TABLE 2.6. Classes of non-stoichiometric compounds

Class	*Example*
(*i*) Cation deficiency	FeS, FeO, CoO, NiO, Cu_2O, CuI
(*ii*) Anion deficiency	NaCl, KCl, KBr
(*iii*) Interstitial cations	UO_2
(*iv*) Interstitial anions	ZnO, CdO

However, the non-stoichiometry is significantly marked in certain compounds, (Table 2.7).

TALBE 2.7. Examples of non-stoichiometric compounds

Hydride	*Oxide*	*Sulphide*	*Other*
$TiH_{1.73}$	$Fe_{0.91-0.95}O$	$Fe_{0.86}S$	$Cu_{1.8}Se$
$PdH_{0.6}$	$Ti_{0.69-1.33}O$	$CrS_{0.95-1.5}$	$Cu_{1.65}Te$
$ZrH_{1.69}$	$Cu_{1.998}O$	$Cu_{1.7-1.96}S$	$Na_x WO_3$
$CeH_{2.7}$	$Ni_{1.996}O$	$CuFeS_{1.94}$	AgI

Pure silicon and germanium are semiconductors. Their semiconductivity is attributed to the displacement of parent atom by a small amount of impurity. Extremely pure specimens of germanium or silicon contain no free electrons as four valence electrons of each atom are held strongly in covalent bonds formed with their adjacent atoms. These two elements, therefore, behave as non-conductors. As already discussed, the introduction of some foreign material as impurity in the regular lattice makes a substance a semiconductor by providing additional energy levels between more widely spaced levels. Addition of 10^{-6} parts of arsenic or antimony (group 15 metals) with five valence electrons into the tetrahedral lattice of germanium or silicon imparts one free electron to the lattice which is not held up in a covalent bond and is free to move under the influence of electrical field [Fig. 2.25 (*b*)]. As a result, conductivity is increased by 50 times. In the energy level diagram three electrons lie close to the conduction band and are easily excited thermally into that band, leaving holes into which other electrons can move. This type of extrinsic semiconductor is known as an *n*-type (*n* for negative) since conduction is increased by the negative electrons.

However, doping the semiconductor crystal such Si or Ge with a which has one electron less with a group 13 elements (B, Al, Ga, In) than the host crystal requires for bonding, leaves an electron vacancy or hole [Fig. 2.25 (*c*)]. Such a defect is referred to as creation of 'positive hole', in the lattice. Under the influence of electrical potential, positive hole is created through the transfer of an electron from a nearby atom into the site of electron vacancy. Such extrinsic semiconductors are known as *p*-type semiconductors (*p* for positive, although there is no positive charge). The holes are energy levels into which valence band electrons can easily be excited so that conduction can occur.

Semiconductors, used in transistors and in rectification and amplification of electron circuits, have revolutionized the communications and computer network.

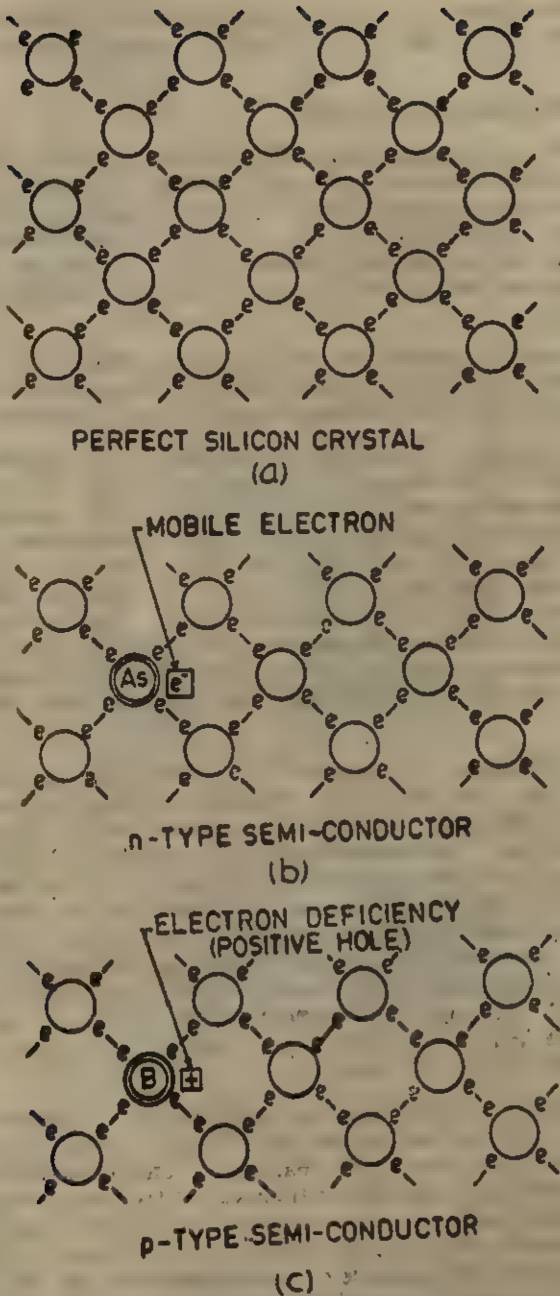


Fig. 2.25. Types of semiconductors : (a) Perfect silicon crystal. (b) Excess electron semiconductor, n-type, and (c) Electron deficient semiconductor, p-type.

A combination of n and p type semiconductors is used in solar cells for the direct conversion of radiant energy into electrical energy.

2.7. PROPERTIES OF SOLIDS

Most solids are characterized by compact ordered arrangements of particles with very restricted motion. Particles in the solid state are unable to move freely past one another, and only vibrate above fixed positions. As a result, solids assume definite shapes. Since the particles are so close together, solids are nearly incompressible and dense. Solid particles do not diffuse readily into other solids.

Some other properties of solids are dependent upon the strength of the attractive forces within the crystals and compositions. Nature of forces also differ from one type of crystal to another.

Melting point. The melting point of a solid is related to the lattice forces. The stronger the attractive forces in the crystal, the greater the kinetic energy is to be assumed by the particles to overcome these forces, and therefore, the higher is the melting point. Ionic crystals have higher melting points than those of molecular crystals but lower than the melting points of covalent network crystals (possess the strongest attractive forces). This is because, the electrostatic attractions between ions are generally much stronger than intermolecular forces. In metallic crystals, the strengths of the attractive forces vary widely hence their melting points cover a wide range.

Heat of fusion. When a solid is heated, the temperature of the solid rises until the melting point is reached. At this stage, any additional heat does not cause a temperature increase. Temperature increases when the process of melting is complete. The heat energy necessary to bring about melting or fusion is called the heat of fusion. The heat energy is used to overcome the attractive forces holding the particles (ions, atoms or molecules). The heat of fusion is a measure of the intermolecular (ionic or atomic) forces of attraction in the solid state. Heats of fusion are usually higher for substances with high melting points than for those with low melting points. Figure 2.26 gives an idea about the various stages involved in the melting of a solid.

Hardness. It varies with the crystals type. Covalent network crystals are very hard because of the large number of strong covalent bonds (Diamond is the hardest). Ionic crystals are also quite hard. They show a greater brittleness and tendency to fracture by cleavage than covalent network solids. Molecular crystals are comparatively soft. Metals range from very hard to soft. Metallic crystals, because of the presence of mobile electrons, can be deformed. They possess the properties of malleability and ductility.

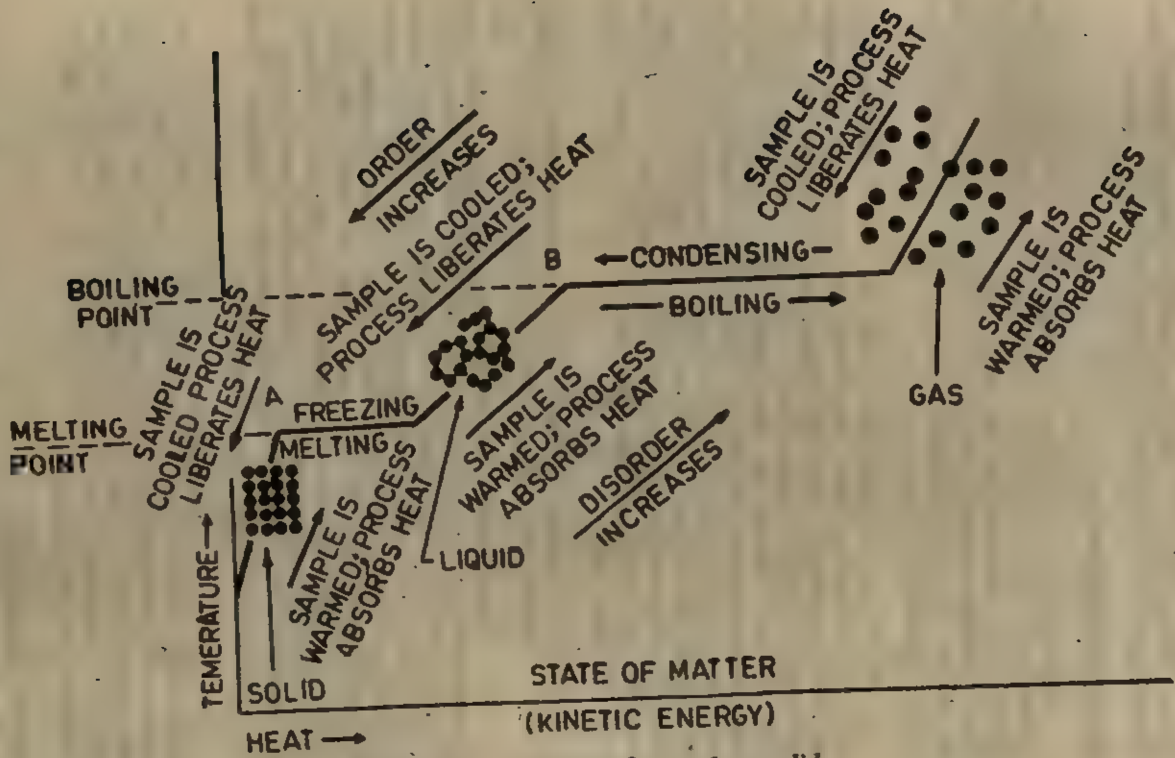


Fig. 2.26. The heating curve for a solid.

Vapour pressure. Of all the types of solids, molecular crystals are the only ones that have an appreciable vapour pressure at room temperature. This is because of the weak intermolecular forces present in these crystals which can be easily overcome.

Electrical conductivity

Conductivity of solids can vary from $10^{-6} \Omega^{-1}$ cm^{-1} in metals to 10^{-22} Ω^{-1} cm^{-1} in insulators. On the other hand semiconductors possess conductivities lying in the range 10^{-2} to $10^{-9} \Omega^{-1}$ cm^{-1}. Thus, based on the relatives values of conductivity, the solids can be classified into three categories, (*a*) metals, (*b*) semiconductors, and (*c*) insulators.

In metals, the presence of free electrons is responsible for high conductance. These free electrons act as charge-carriers and are capable of migration under the influence of electric field resulting in the high conductivity of metals. These electrons can move without destroying the crystal lattice. These displaced electrons take new positions by displacing neighbouring electrons and so on. In the other three crystal types, the electrons are all too tightly bound to permit delocalized motion. Although ionic crystals are non-conductors, ionic substances in the liquid state will conduct electricity. In the liquid state, the electrical charge can be carried by the motion of ions.

Graphite (a mixture of molecular and covalent network crystal forms) is an exception in that it is an electrical conductor.

Many compounds in the solid state are insulators since these do not contain significant number of charge-carriers. The conductivity of solids can be attributed to the migration of charge-carriers like, electrons, ions, vacancies, charged interstices existing in the conducting solids. A perfect crystal of ionic solid like NaCl or KCl cannot conduct electricity to any significant extent. However, it is interesting to note that the presence of impurities or other imperfections in these substances can increase the conductivities of these insulators to very high values by producing desirable defects so that these can be used as semiconductors.

The conductivity increases with increase in temperature because defects in solids also increase when thermally excited. Defective crystals—oxides and sulphides of transition and some other heavy metals have assumed an ever increasing importance in modern technology because of their high conductivity. Such solids are classified as semiconductors.

Magnetic impurities

Solids can be classified into different classes depending on their response to magnetic fields. Diamagnetic materials (*e.g.*, TiO_2,

NaCl, benzene) are weakly repelled by magnetic fields whereas paramagnetic materials are attracted by magnetic fields. They, however, donot show magnetic properties in the absence of magnetic field. Atoms, molecules and ions with unpaired electrons are paramagnetic substances and always show magnetic properties. There is a third category of solids which show permanent magnetism even when the magnetic field is absent (*e.g.*, Fe, CrO_2). Such substances are called ferromagnetic substances. Iron, cobalt and nickel show ferromagnetism at room temperature. Once such a material is magnetised, it remains permanently. All magnetically ordered materials acquire paramagnetic nature at high temperature due to randomness of spins of their electrons. Ferrimagnetic Fe_3O_4 acquires paramagnetic properties at 850 K.

Dielectric properties

As we know insulators do not conduct electricity because of non-availability of electrons for carrying charge. However, the separation of charges create dipoles : (*i*) Allignment of these dipoles may either lead to net dipole moment, or (*ii*) the dipole moments cancel each other. (*iii*) There is another possibility that there is hardly any dipoles in the crystal. Crystals in which the situation (*i*) is assumed exhibit **piezoelectricity**. Mechanical deformation of such crystals lead to the generation of electricity due to the displacement of ions. On the other hand the application of electrical field leads to atomic displacements causing mechanical strain. Thus, a piezoelectric crystal acts as a mechanical transducer. Such crystals find use as pickups in record players.

2.8 AMORPHOUS SOLIDS

All solids are not crystalline. There are solids which have no well defined ordered structures. Such solids have no definite melting point and definite heat of fusion. Examples are rubber, glass, fused silica and polymers of high molecular masses such as plastic, starch *etc*. These are termed as amorphous substances.

The detailed studies by X-ray diffraction methods reveal that an ordered arrangement of particles is not present in amorphous substances, as a result of which these do not possess a definite geometry and shape. The crystalline solids possess long-range order extending over the entire crystal, whereas in amorphous solids there is no long range order. The amorphous solids can be regarded as **pseudo solids**. The rigidity of amorphous substance is only apparent, *e.g.*, in very ancient buildings it is found that the glass window panes are thicker at the bottom and thinner at the top ends, as if the glass is not rigid but flowing down on account of its own mass. But the rate of flow is so slow that it may take years for a significant flow to occur. The arrangement of the constituent particles of amorphous substances is more like liquids, which contain only short range order, and it possesses more disorder than crystalline solids. As a result, the amorphous substances are **isotropic**, *i.e.*, the properties like

electrical conductivity, refractive index *etc.*, are same, no matter in which direction we measure these properties. In this the respect amorphous substances resemble gases and liquids.

At times amorphous solids acquire both crystalline and non-crystalline characteristics. Amorphous solids on heating become crystalline at some temperatures, but left to themselves under ordinary conditions they remain amorphous. Because of this property, objects from ancient civilisations are still with us, although some of them may have assumed milky appearance (instead of being transparent) because of some crystallization. Another common amorphous solid is sulphur. On quenching molten sulphur (S_8) at room temperature, an open helix amorphous form is obtained. Over a long period it reverts to rhombic crystaline form of sulphur.

Amorphous solids find many applications because of their unique properties, the obvious ones being of the inorganic glasses, in construction, house-ware, laboratory-ware, *etc.* Amorphous silica is likely to be the best material for converting the sunlight into electricity (photovoltaic).

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

2·1 Choose the correct answer out of the four alternatives given for the following questions :

(*i*) Which of the following properties of solids is true ?

(*a*) The coordination number of an atom in hexagonal closest-packing is higher than in body centred cubic packing.

(*b*) Ionic solids are low melting soft crystalline compounds.

(*c*) Metallic crystals are hardly good conductors of heat and electricity.

(*d*) Ionic solids do not have definite melting point and heat of fusion.

(*ii*) Which of the following compounds assume face centred cubing lattice ?

(*a*) CsCl (*b*) ZnS

(*c*) CaF_2 (*d*) NH_4Cl

(*iii*) Which of the following properties do not characterize the solids ?

(*a*) definite melting point (*b*) definite heat of fusion

(*c*) definite crystal lattice (*d*) weak chemical bonding

(*iv*) Which of the following impurity added to silicon would form an *n*-type semiconductor ?

(*a*) P (*b*) Al

(*c*) C (*d*) none

(*v*) Which of the following impurity added to silicon would form a *p*-type semiconductor ?

(*a*) As (*b*) S

(*c*) B (*d*) Ge

(*vi*) In which of the following solid substances, the cations occupy octahedral voids ?

(*a*) NaCl (*b*) ZnS

(*c*) CaF_2 (*d*) ZnO

(*vii*) Which of the following species suffer from metal excess defect ?
(*a*) ZnO (*b*) FeO
(*c*) AgCl (*d*) FeS

(*viii*) Which of the following silicates contain SiO_4^{4-} anion ?
(*a*) albite (*b*) phenacite
(*c*) silica (*d*) talc

(*ix*) In which of the following silicates one oxygen is shared between two tetrahedra ?
(*a*) zircon (*b*) asbestos
(*c*) zeolite (*d*) thortveitite

(*x*) Which of the following compounds has maximum interionic distance ?
(*a*) CsF (*b*) NaF
(*c*) CsCl (*d*) KI

2.2 Fill in the blanks with the appropriate words :

(*i*) Sodium chloride crystallizes in the.........system.

(*ii*) A regular three dimensional arrangement of the identical points or particles in space constitutes a.........

(*iii*) The intentional incorporation of an impurity into a crystal is termed ....

(*iv*) A.........is a substance that does not conduct electricity well at room temperature but does at higher temperatures.

(*v*) The fluorite structure is named after the mineralogical name for...... ....

(*vi*) In the zinc blende structure, positive ions fill only.........holes in a ....array of negative ions.

(*vii*) The radius ratio $\frac{r_c}{r_a}$ of ions in a crystal determines the.........of the ions and hence the type.........formed.

(*viii*) A non-crystalline solid with no well-defined ordered structure is called.........

(*ix*) ....is a fibrous silicate with either the chain or sheet structure.

(*x*) In a.........the migration of cation and anion from their lattice sites to the surface of a crystal takes place.

2.3 Choose the true (T) and false (F) statements out of the following :

(*i*) The properties of solids depend upon the bonding forces between the particles at the lattice points of the crystal.

(*ii*) Electrical neutrality is never maintained in non-stoichiometric crystals.

(*iii*) Ionic crystals are high melting but brittle and fracture easily under pressure.

(*iv*) Metals are composed of close-packed neutral atoms surrounded by delocalized valence electrons.

(*v*) In both sodium chloride and zinc sulphide, the anions are in a face centred cubic system : the Na^+ ions occupy tetrahedral holes in NaCl and the Zn^{2+} ions fill both octahedral and tetrahedral holes.

(vi) The lattice energy is the energy released in the formation of the solid crystal form the gaseous ions.

(vii) Silicon and germanium are semiconductors whose electrical properties change when a small amount of group 13 elements or a group of 15 elements is added.

(viii) A common error is to describe the CsCl lattice as body centred cubic.

(ix) The lattice points of CaF_2 consist of the eight corners and the six face centred positions (the site of Ca^{2+} ions) as well as the eight tetrahedral holes (the location of the fluoride ions).

(x) Crystals contain many imperfections that have important effects on their properties.

2.4 Match the items under column B against the items given under the column A.

	Column A		Column B
(i)	A crystal	(a)	is a periodic repeating array of units with identical environments about each similar unit.
(ii)	A lattice	(b)	tetrahedral holes
(iii)	NaCl	(c)	AgCl
(iv)	CaF_2	(d)	NH_4Cl
(v)	face centred cubic system	(e)	is a solid with well defined planar surfaces
(vi)	zinc blende structure	(f)	Na_2O
(vii)	body centred cubic system	(g)	octahedral holes
(viii)	Wurtzite structure	(h)	CuCl
(ix)	antifluorite structure	(i)	ZnO
(x)	caesium chloride structure at high pressure	(j)	NH_4I

SHORT ANSWER QUESTIONS

2.5 (i) MgO has the structure of NaCl and TlCl has the structure of CsCl. What are the coordination numbers of the ions in MgO and TlCl ?

(ii) Suppose a particular metal crystallizes in three different polymorphs body centred cubic, *hcp*, and simple cubic.

(a) Which polymorph would be the densest ?

(b) Which would be the least dense.

(iii) The density of two metals will always be inversely proportional to the unit cell volume Comment.

(iv) What is the essential difference between the bonding in Na_2 molecule and in solid sodium ?

(v) State the difference between the three cubic unit cells.

(vi) Describe the lattice assumed by the following : KCl, BaO and CuCl.

(vii) Distinguish between *n*- and *p*-type semiconductors.

(viii) Which of the following impurities added to silicon would form *n*-type semiconductor ? Which would form a *p*-type semiconductor ?

(a) P, (b) Ga (c) As. (d) Te

(e) Se.

(*ix*) Explain why the electrical conductivity of a semiconductor increases at higher temperatures ?

(*x*) Explain why the electrical conductivity of an ionic compound decreases at lower temperatures. Explain with the help of examples from covalent solids and metals.

TERMINAL QUESTIONS

2.1 Describe the main characteristics of a crystalline solid and an amorphos solid.

2.2 Classify the solids on the basis of rotational symmetry of the unit cell.

2.3 What is meant by the primitive and non-primitive unit cell ?

2.4 Explain the following :

(*a*) an edge (*b*) a plane
(*c*) space lattice (*d*) unit cell of a crystal

2.5 Describe the packing system of hexagonal and cubical closest packed structures. What types of voids are present in these structures ? Give the number of voids for closest-packed atom.

2.6 What are the *hcp* and *fcc* arrangements in crystals ?

2.7 Draw the diagrams of *hcp*, *bcc* and *fcc* arrangements in ionic solids. Give the examples of ionic substances which are found in these packings.

2.8 Describe the unit cell of sodium chloride and explain its features.

2.9 What is meant by crystal defects ? What is a dislocation ? Distinguish between an edge dislocation and a screw dislocation.

2.10 What is a semiconductor ? Describe the two main types of semiconductors and contrast their conduction mechanisms.

2.11 How does the presence of (*a*) Schottky defects, and (*b*) Frenkel defects affect the density of a crystal ?

2.12 What are non-stoichiometric crystals ? Describe the defects observed in them.

2.13 What do you mean by intrinsic and extrinsic defects in crystalline solids? What is the nature of defects in natural gems ? What are the different types of point defects ?

2.14 Illustrate with examples, the Schottky and Frenkel defects. What types of defects result in change of the stoichiometric composition of the substance, and why ?

2.15 How do you explain the increase in electrical conductivity of crystalline solids in presence of defects due to presence of different types of impurities ? How do you visualise the electrical conductivity of metals ?

2.16 (*a*) Illustrate with a diagram that conductance in silicon crystal containing third group element impurity, is due to the migration of the electrons and vacancies in opposite directions under the influence of electric field.

(*b*) What are the relative values of electrical conductivities of (*i*) conductors, (*ii*) insulators, and (*iii*) semiconductors ?

2.17 Descibe the differences in island, chain and sheet structures of silicates. What type of silicate structures are present in asbestos and clay materirals ?

2.18 Describe the properties of solids.

2.19 A metal with atomic mass 40.08 amu forms a cubic closest packed crystal whose unit cell is 5.576×10^{-8} cm on a side. Calculate its density. (Ans. 1.55 g cm^{-3})

2.20 The measured density of face centred cubic crystalline copper is 8.6 g cm^{-3}. Calculatethe unit cell edge length. (Ans. 3.61 Å)

ANSWERS TO SELF ASSESSMENT QUESTIONS

2.1 (*i*) a (*ii*) b (*iii*) d (*iv*) a (*v*) c (*vi*) a (*vii*) a (*viii*) b (*ix*) d (*x*) c.

2.2 (*i*) face-centred cubic (*ii*) crystal lattice
(*iii*) doping (*iv*) semiconductor
(*v*) calcium fluoride (*vi*) one-half of tetrahedral ; cubic closest packing (ccp)
(*vii*) Coordination number ; crystal structure (*viii*) amorphous solid
(*ix*) Asbestos (*x*) Schottky defect.

2.3 (*i*) T (*ii*) F (*iii*) T (*iv*) T (*v*) F (*vi*) T (*vii*) T (*viii*) F (*ix*) F (*x*) T.

2.4 (*i*) e (*ii*) a (*iii*) g (*iv*) b (*v*) c (*vi*) h (*vii*) d (*viii*) i (*ix*) f (*x*) j

2.5 (*i*) MgO : each ion is surrounded by six nearest neighbours of the opposite nature. Hence coordination number of each ion is six

TlCl : each ion is at the centre of cube. Hence, coordination number of each ion is eight.

(*ii*) (*a*) hcp (*b*) simple cube

(*iii*) The statement is true. The cell with a small volume say *ccp* will have the smallest free space for a regular array of atoms of one size, hence the density will be higher for the metal which adopts this type of unit cell.

(*iv*) The bonding in the Na_2 molecule is covalent. In sodium metal, the bonding is metallic. In the Na_2 molecule the electrons are localized while in the case of sodium metal they are not.

(*v*) The simple cubic unit cell contains eight units, one at each corner. The body centred cube is identical with additional one unit in the centre of the cube. The face centred cube has six units more than the simple cube, one in the centre of each of the six faces.

(*vi*) KCl and BaO assume sodium chloride lattice. CuCl assumes zinc blende structure.

(*vii*) If a group 15 element say P is added to silicon before it crystallizes, it has one extra electron than is required for bonding in the host crystal (Si). This extra electron can move through the crystal providing conductivity. This type of semiconductor is known as *n*-type since conduction is increased by the negative electron given by group 15 element.

Doping the semiconductor crystal with a group 13 element (B, Al, *etc.*), which has one electron less than a silicon host crystal requires for bonding, leaves an electron hole. This semiconductor crystal is labelled p-type as the electron hole migrate toward a cathode as electrons from neighbouring atoms flow into the vacant bond positions.

(*viii*) (*a*) n-type (*b*) p-type (*c*) n-type (*d*) n-type (*e*) n-type

(ix) The conductivity of a semiconductor increases with increasing temperature because an increasing number of electrons has sufficient thermal energy to occupy the conduction band.

(x) Most of the ionic substances conduct electricity only in the liquid state and covalent substances do not conduct either in the solid or in the liquid state. A metal conducts electricity in both the solid and liquid states.

In a ionic solid the ions are not free to move in the solid state; in the liquid state the ions can move. On cooling the molten ionic solid, the speeds of the ions decrease. AgH result, under the influence of an applied electric current, the distance travelled by the ions in a given time decreases with decreasing temperature. Hence, the conductivity decreases.

In a metal, on the other hand, the electrons (small and light) move at very high speeds even at low temperatures.

A covalent solid has no ions and the electrons are not free to move as they are held firmly to the atoms.

□ □

UNIT 3

Solutions

Almost all the chemical processes which occur in nature, whether is animal or vegetable organisms, or in the non-living surface of the earth,..............take place between substances in solution.

—W. OSTWALD, 1890

UNIT PREVIEW

3.1 Introduction
3.2 Expressions of concentrations
3.3 Types of solutions
3.4 Gaseous solutions
3.5 Liquid solutions
  3·5·1 Solutions of gases in liquids
  3·5·2 Solutions of liquids in liquids—ideal solutions and non-ideal solutions
  3·5·3 Solutions of solids in liquids—colligative properties
3.6 Molecular mass determination
3.7 Solid solutions
3.8 Electrolyte solutions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Define the terms solution, solute, solvent, solubility and saturated solution.
2. Distinguish between the strength and concentration of a solution,
3. Define the expressions of concentration : calculate concentrations in units of mass percentage, mole fraction, molality or molarity, and convert concentrations from one unit to another.
4. Give examples of different types of solution.
5. Explain the process by which solutes dissolve in solvents to form solutions and the enthalpy changes which accompany this process.
6. Explain the effects of changing temperature and pressure on the solubilities of solutes.
7. Distinguish between weak and strong electrolyte.
8. State the Dalton's law of partial pressure, Henry's law and Raoult's law.
9. Describe the nature of solution of liquids in liquids in terms of ideal and non-ideal behaviour.
10. Explain the meaning of the term colligative properties and predict the effect of electrolytes on them.
11. Predict the effect of the concentration of non-volatile solutes on the vapour pressure, boiling point, freezing point, and osmotic pressure of solution.
12. Describe the experimental procedures for the measurement of colligative properties of solutions and use these properties to calculate the molar masses of solutes.

3.1 INTRODUCTION

Solutions are familiar to all of us. The water we drink is a solution of various minerals dissolved in water. Plants derive their food, in part, from the water soluble constituents of the soil. The food we take is converted into soluble substances, through chemical reactions. Blood absorbs these soluble substances and finally are carried to various tissues in the body. The air we breathe in is a solution of nitrogen and oxygen gases. Aquatic life derives the oxygen necessary for its life process from oxygen dissolved in water.

Many chemical reactions are performed in solution, since the rate of reaction in a solution may be faster than between the substances in their native state. This is perhaps due to the better contact of the reactants with each other.

Solutions are like compounds in that they are homogeneous, and they are like mixtures in that the relative proportions of the constituents are variable.

Many familiar solutions comprising variable proportions of constituents have been mentioned in the beginning of this unit. Other familiar solutions are—a soft drink, brass, stainless steel, dental fillings, brine, *etc.*

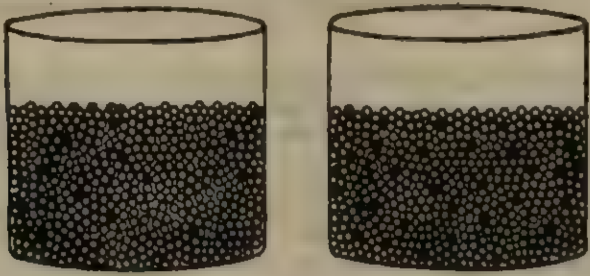
A solution is a homogeneous mixture of two or more substances. Several types of solutions exist, but in this unit we will consider solutions obtained by mixing only two substances. In some cases, there is a limit to the amount of solute that will dissolve in a given amount of solvent. When this limit is reached, a **saturated solution** is formed, this being defined as one which, at a given temperature, is in equilibrium with undissolved solute. A true solution consists of a solvent and one or more solutes whose proportions can vary from solution to solution. The essential feature of a solution is that the solute is dispersed in the solvent as individual molecules or ions, so that a true solution consists of a single phase.

The solubility of a substance in another one, besides depending upon their nature, is affected by temperature and pressure changes, although the latter is important only in the case of solubility of gases.

The terms solute and solvent are used in connection with solutions, and it is the solute which is dissolved by the solvent, the latter being the substance which is present in excess. This type of classification is not justified if the two substances are present in equal amounts. In such a case, any of the two can be taken as solvent or solute depending upon the convenience. However, in connection with the solution of a solid in a liquid, the latter is always referred to as the solvent.

3.2. EXPRESSIONS OF CONCENTRATION

When substances are soluble to a considerable extent, a solution may contain a large amount of solute (concentrated) or a small amount of solute (dilute) in the same amount of solvent. The concentration of a solution is the ratio of the amount of solute to the amount of solvent or solution. Two concentrations of a solution are shown in Fig. 3.1.



(a) DILUTE SOLUTION (b) CONCENTRATED SOLUTION

Fig. 3.1. (a) A dilute solution (less concentrated) : the ratio of solute to solvent molecules is smaller.

(b) More concentrated solution : the ratio of solute to solvent molecules is higher than in (a).

In order to give the precise meaning to the solubility it is necessary to specify the quantities of solute and solvent that are present in a solution. The relative amounts of solute and solvent in a solution can be expressed quantitatively in terms of mass, moles or volume. Some of the commonly used expressions of concentration are summarized in Table 3.1.

TABLE 3.1. Some common ways of expressing concentrations of solutions.

Name	*Abbreviation*	*Definition*
Mass per cent	mass %	Parts by mass of solute per 100 parts by mass of solution; usually g per 100 g of solution.
Volume per cent	vol %	Parts by volume of solute per 100 parts by volume of solution; usually 1 mL per 100 mL of solution.
Parts per million	ppm	Parts by mass (or volume) of solute per 10,00,000 parts by mass (or volume) of solution.
Molarity	*M*	Number of moles of solute per litre of solution.
Molality	*m*	Number of moles of solute per kilogram of solvent.
Mole fraction	*x*	Ratio of moles of a component per total moles.
Normality	*N*	Number of equivalents of solute per litre of solution.

Since the density of a solution varies with temperature, presumably due to the variation of volume, it is obvious that molarity of a solution varies with temperature, while its molality and mole fraction will remain independent of temperature. Here, we shall consider the relations among expressions of concentrations. Throughout we shall use subscript 1 to represent solvent and subscript 2, for the solute.

Mass per cent.

In only a few cases, percentage concentrations involve volumes of either solute or solvent, *e.g.*, solutions of gases or solutions of liquids. Mass per cent expression is quite common. A 20% solution contains 20 g of a solute dissolved in 100 g of solution. The total mass of the solution is equal to the mass of the solute plus the mass of the solvent, *i.e.*, 100 g of the 20 per cent solution contains 20 g of solute and 80 g of solvent.

$$\text{Per cent concentration} = \frac{\text{mass of solute}}{\text{total mass of solution}}$$

$$= \left(\frac{\text{g solute}}{\text{g solute} + \text{g solvent}}\right) \times 100$$

Molality and mole fraction

Generally the concentration of solute in dilute solutions is expressed in mole fraction. An expression of concentration used for concentrated solution is molality, *m*. Molality is the number of moles of solute contained in 1 kg of solvent, *i.e.*,

$$\text{Molality, } m = \frac{\text{moles of solute}}{\text{kg of solvent}} \text{ mol kg}^{-1}$$

i.e., Amount m solute is present kg of solvent

The most fundamental expression of concentration on a molecular basis is **mole fraction**, since the number of moles of each component is considered.

The mole fraction, x of a component in a solution is the fraction of the total number of moles in the solution contributed by a particular component.

Mathematically, the mole fraction of solute x_2 will be

$$x_2 = \frac{n_2}{n_1 + n_2 + n_3 + \ldots\ldots}$$

This fraction can be used with gaseous liquid or solid solutions and being a fraction, it has no units.

If M_1 is the molar mass of the solvent, the amount of solvent in the solution of molality m will be

$$n_1 = \frac{1 \text{ kg}}{M_1}$$

Hence, total amount of solute and solvent in solution

$$= \text{amount of (solute+solvent)}$$

$$=n_2+n_1=m+\frac{1\text{ kg}}{M_1}$$

Hence, the mole fraction of solute x_2 will be

$$x_2=\frac{n_2}{n_1+n_2}=\frac{m}{m+\dfrac{1\text{ kg}}{M_1}}$$

For dilute solutions where $n_1 < n_2$, the expression becomes

$$x_2=\frac{m}{\dfrac{1\text{ kg}}{M_1}}$$

that is, mole fraction of solute is proportional to the molality of the solution.

Now it is clear that molality differs from the mole fraction, then, in being based on a mass of solvent rather than on the total number of moles in the solution.

Molality and Molarity

We have already discussed the concept of molality and its relation with mole fraction.

Molarity is an expression of concentration based on the volume of solution. The molarity M of a solution is the number of moles of solute per litre of solution, *i.e.*,

$$M=\frac{\text{moles of solute}}{\text{litres of solution}}\text{ mol dm}^{-3}$$

The relationship between the molarity and molality of a solution depends on the density of the solution. When water (density $\rho=1.00$ g/mL) is the solvent, dilute solutions contain nearly 1000 g of water per 100 mL and the molarity and molality are almost the same. At concentrations of $>$1·00 M, the difference is significant With solvents having densities much different from that of water, the difference between molarity and molality will be even larger than is with aqueous solutions.

Suppose V be the total volume of the solution and P be its density. If M_2 is the molar mass of the solute, and its amount m is present in 1 kg of the solvent, then

Total mass of solution = mass (solute + solvent)

$$=m\,M_2+1\text{ kg}$$

The volume of the solution

$$V=\frac{m\,M_2+1\text{ kg}}{P}$$

Now the definition of molarity, M is as follows :

$$\frac{m}{V}=\frac{m\,L}{m\,M_2+1\text{ kg}}$$

Molarity and Mole fraction

Total mass of 1 L (dm^3) solution will be,

$$m_{total}=\rho(1\text{ L})$$

Mass of the solute m_2 in this solution will be,

$$m_2=MM_2$$

where M is the molarity and M_2 is the molar mass of solute.

Mass of the solvent m_1 will be

$$m_1=m_{total}-m_2$$
$$=\rho(1\text{L})-MM_2$$

Amount of solvent will be,

$$n_1=\frac{m_1}{M_1}=\frac{\rho(1\text{L})-MM_2}{M_1}$$

Therefore $\quad x_2=\dfrac{n_2}{n_1+n_2}$

$$=\frac{M}{\dfrac{\rho(1\text{L})-MM_2}{M_1}+M}$$

$$=\frac{MM_1}{\rho(1\text{L})+M(M_1-M_2)}$$

In case of dilute solutions, $n_2 \ll n_1$ *i.e.*, $MM_2 \ll \rho(1\text{L})$ and $\rho_{solution}$ is almost equal to $\rho_{solvent}$, and the expression becomes

$$x_2=\frac{MM_1}{\rho(1\text{L})}\quad\text{or}\quad\frac{MM_1}{\rho(1\text{ dm}^3)}$$

that is, the mole fraction of solute x_2 is directly proportional to the molarity M of the solution.

Exercise 3.1. *What is the molality of 20 mass per cent aqueous H_2SO_4 solution ?*

Solution : In the solution of H_2SO_4, we have

Mass of H_2SO_4, $\quad m_2=20$ g

Mass of water, $\quad m_1=80$ g

The molar mass of H_2SO_4, $M_2=98$ g mol^{-1}

Amount of H_2SO_4 in 20 g, $\quad n_2=\dfrac{m_2}{M_2}=\dfrac{20\text{ g}}{98\text{ g mol}^{-1}}$

$$=0.204\text{ mol}$$

0.204 moles of H_2SO_4 are present in 80 g of water

Therefore $\quad m=\dfrac{0.204\text{ mol}}{80\text{ g}}\times\dfrac{1000\text{ g }H_2O}{1\text{ kg }H_2O}$

$$=2.6\text{ mol kg}^{-1}$$

Exercise 3.2. *Calculate the mole fraction, molality and molarity of a solution containing 10 mass per cent H_2SO_4 in water. The density of resultaut solution is 1.07 g/cm³.*

Solution : In 100 g of solution, we have

Mass of H_2SO_4, $m_2=10$ g

Mass of water, $m_1=90$ g

Molor mass of H_2SO_4, $M_2=98$ g mol^{-1}

Amount of H_2SO_4 in 10 g,

$$n_2=\frac{m_2}{M_2}=\frac{10\text{ g}}{98\text{ g mol}^{-1}}$$
$$=0.102\text{ mol}$$

Amount of water in 90 g,

$$n_1=\frac{m_1}{M_1}=\frac{90\text{ g}}{18\text{ g mol}^{-1}}$$
$$=5\text{ mol}$$

Mole fraction of H_2SO_4,

$$x_2=\frac{n_2}{n_1+n_2}$$
$$=\frac{0.102\text{ mol}}{(5+0.102)\text{ mol}}$$
$$=0.02\text{ mol}$$

Molality of H_2SO_4 solution,

$$m_2=\frac{n_2}{m_1}=\frac{0.102\text{ mol}}{90\times10^{-3}\text{ kg}}$$
$$=\frac{0.102\times1000\text{ mol kg}^{-1}}{90}$$
$$=1.34\text{ mol kg}^{-1}$$

The solution contains 10 g H_2SO_4 in 100 g of solution whose volume will be,

$$V=\frac{\text{mass of solution}}{\text{density of solution}}$$
$$=\frac{100\text{ g}}{1\cdot07\text{ g}}=93.5\text{ cm}^3$$

Therefore, molarity of H_2SO_4 solution,

$$M=\frac{n_2}{V}=\frac{0.102\text{ mol}}{9.35\text{ cm}^3}\times\frac{1000\text{ cm}^3}{1\text{ dm}^3}$$
$$=1.09\text{ mol }dm^{-3}$$

3.3. TYPES OF SOLUTIONS

Solutions may involve many different combinations in which solid, liquid or gas acts as either solvent or solute. Solvents and

solutes mix homogeneously to form solutions. In any solution, the dispersed particles are no longer part of their original solid, liquid or gas. For example, the condition of alcohol molecules in water is not much different from that of sugar molecules in water. In both the cases the solute has disappeared. Based upon this observation, it will be better to consider that there are only three types of solutions : solid, liquid and gaseous (Table 3.2).

TABLE 3.2 Types of solutions

Solution type	*Example*
Gaseous solutions	
Gas dissolved in gas	Air : oxygen dissolved in nitrogen
Liquid dissolved in gas	Chloroform dissolved in (evaporated into) nitrogen ; water vapour in air
Solid dissolved in gas	Camphor in air ; dry ice dissolved in (sublimed into) nitrogen ; iodine vapour in air
Liquid solutions	
Gas dissolved in liquid	CO_2 dissolved in water ; mine ral water
Liquid dissolved in liquid	Alcohol dissolved in water, benzene in toluene
Solid dissolved in liquid	Common salt dissolved in water ; sugar in water
Solid solutions	
Gas dissolved in solid	Hydrogen adsorbed in palladium
Liquid dissolved in solid	Mercurry dissolved in zinc or gold
Solid dissolved in solid	Alloys like brass (zinc dissolved in copper)

3.4. GASEOUS SOLUTIONS

All gases mix in all proportions to yield a homogeneous gaseous mixture. Any gaseous phase, no matter how many gases of different types are mixed in it, can be termed as a gaseous solution. One of the most familiar examples is air which can be regarded as a gaseous solution of the gases—nitrogen, oxygen, argon, carbon dioxide, *etc.* contained in air. The physical picture of a gaseous solution can be regarded similar to that of a pure gas with the only difference that instead of molecules of the same kind present in a pure gas, different kinds of molecules are contained in it.

Liquids and solids in the gaseous states disperse with ease to form nearly ideal solutions under normal conditions of temperature and pressure provided no chemical interaction occurs. Gas molecules diffuse to form homogeneous mixtures and mix in all proportions as they are widely separated and possess high kinetic energies. In such solutions (mixtures), gas molecules behave independently and exert pressure in proportion to the number of molecules of that type

present in mixture. Their compositions may be easily expressed in terms of their partial pressures or mole fractions.

3.5 LIQUID SOLUTIONS

3.5 1 Solutions of Gases in Liquids

Gases are soluble in liquids. For a given pair of gas and liquid solubility depends on temperature and pressure.

At higher temperatures, the solubility of gases in liquids decreases. This is because, gas molecules at higher temperatures gain kinetic energy and escape from solution.

Changing the pressure has hardly any effect on the solubilities of either solids or liquids in liquids. However, gases are more soluble in liquids at higher pressures. Carbonated water is a saturated solution of CO_2 in water under pressure.

Dissolution of gas in a liquid is generally an exothermic process ($\Delta H_{soln.}$ is usually negative). This is because the solvation energy usually exceeds the energy necessary to separate the molecules in the liquid. The extent to which different gases dissolve in a liquid solvent at a fixed temperature and pressure depends upon the intermolecular attraction between the gas and liquid molecules. Solubility is increased to a very high extent if there occurs a chemical interaction between the gas and liquid. Hydrogen bonding between NH_3 and H_2O molecules is responsible for the much greater solubility of NH_3 in H_2O.

$$NH_3+H_2O \rightleftharpoons NH_3.H_2O \rightleftharpoons NH_4^++OH^-$$

Experience shows that polar gases are generally more soluble in polar solvents and non-polar gases are most soluble in non-polar liquids. Hydrogen halides, HF, HCl, HBr and HI are all polar covalent gases and dissolve easily in water giving hydraulic acids. Although CO_2 and O_2 are non-polar gases, they do dissolve to limited extents in water. Carbon dioxide is slightly more soluble because it reacts with water to form H_2CO_3, which, in turn, ionizes.

Thus, the gases that dissolve significantly in water are those that are capable of hydrogen bonding (*e.g.*, NH_3, HF), those that ionize (*e.g.*, HCl, HBr and HI) and those that react with water (*e.g.*, CO_2, SO_2, *etc.*).

Henry's law is applicable to gases that do not react with the solvent in which they dissolve (as well as to some cases in which gases react partially), *i.e.*, for gases whose intermolecular attractions consist of only London forces. The concentration of a gas in a solution is proportional to the partial pressure of the gas above the surface of the solution.

$$C_g=k\,p_g \qquad ...(3.1)$$

where C_g is the concentration of the gas, p_g is the partial pressure above the solution and k is Henry's law constant, the value of which varies with the gas and the temperature.

3.5.2. Solutions of Liquids in Liquids

When a liquid is added in another liquid, it may exhibit any of the three following possibilities :

(*i*) completely miscible pair of liquids which form solutions in all proportions, *e.g.*, water and ethanol ; benzene and toluence ; water and acetone.

(*ii*) completely immiscible pair of liquids which do not mix at all, and form two layers, *e.g.*, water and paraffin oil, water and benzene *etc.*

(*iii*) partially miscible pair of liquids which form solutions over a limited range of concentration, *e.g.*, phenol and water ; water and triethylamine *etc.*

Miscibility refers to the ability of one liquid to mix with another.

The obvious question is why some pairs are completely miscible whereas others are not ? To answer this question we may use the principle of **like dissolves like**, *i.e.*, chemically alike liquids readily dissolve in one another freely, whereas chemically different liquids do not.

Polar water and polar ethanol are miscible, *i.e.*, mutually soluble in all proportions. Non-polar benzene and non-polar toluence (or carbon tetrachloride) have unlimited solubility in one another. However, a polar liquid (H_2O) and a non-polar liquid (benzene) hardly dissolve in one another.

Properties of solutions of liquids in liquids

We will consider the liquids which mix with each other completely over all ranges of composition. Such solutions are classified in two classes : (*i*) ideal solutions, and (*ii*) non-ideal solutions.

(*i*) **Ideal Solutions** Solutions which obey **Raoult's law** under all conditions of composition are known as ideal solutions. According to Raoults law, the partial pressure of the vapour of a constituent of an ideal solution is directly proportional to the product of the mole fraction of the component in the solution and the vapour pressure of the pure component at the same temperature, *i.e.*,

$$p_A = x_A p^\circ_A \quad \cdots(3.2)$$

where p_A = the partial vapour pressure of A above the solution
x_A = the mole fraction of A in the solution
p°_A = the vapour pressure of pure A at the same temperature as the solution.

p°_A is also called a constant of proportionality.

In solutions of liquids in liquids, each liquid has a significant vapour pressure, so the vapour phase over the solution contains molecules of each component (Fig. 3.2).

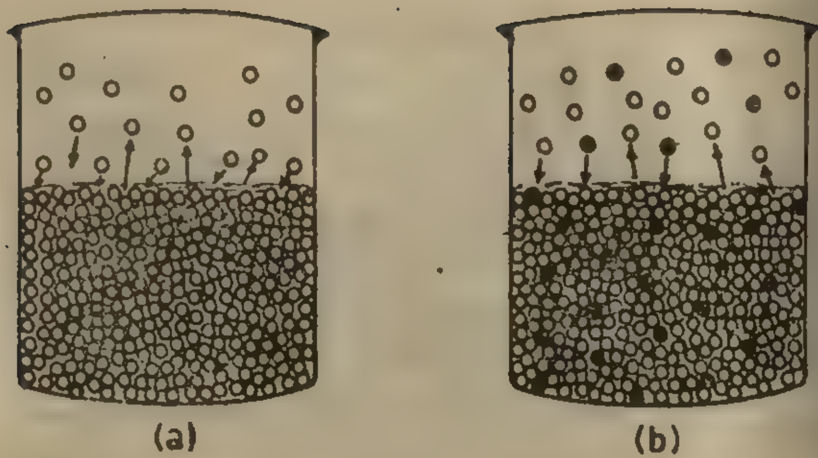


Fig. 3.2. (a) The vapour above a pure liquid, and (b) The vapour above a solution of liquids contains molecules of each component. For an ideal solution, the partial vapour pressure of each liquid will be proportional to the mole fraction of each component.

According to **Dalton's law of partial pressures**, the total vapour pressure of an ideal solution is the sum of the vapour pressure of each component in the vapour phase :

$$p_{total} = p_A + p_B + \ldots\ldots$$

For a binary ideal solution of two liquids A and B, we will have,

$$p_{total} = p_A + p_B \qquad \ldots(3{\cdot}3)$$

Thus, according to Raoult's law is,

$$p_{total} = x_A p^\circ_A + x_B p^\circ_B \qquad \ldots(3{\cdot}4)$$

Since $x_A + x_B = 1$, we will have

$$p_{total} = x_A p^\circ_A + (1 - x_A) p^\circ_B$$

$$= p^\circ_B + (p^\circ_A - p^\circ_B) x_A \qquad \ldots(3{\cdot}5)$$

Since p°_A and p°_B are constants at constant temperature, equation (3.5) suggests that total vapour pressure, p_{total} of the solution is a linear function of the mole fraction of the component A. If we plot p vs. x_A ,we should obtain a straight line with a slope equal to $(p^\circ_A - p^\circ_B)$ and intercept p°_B.

Similarly, we can deduce relationship between the total vapour pressure, p_{total} and the mole fraction x_B as :

$$p_{total} = p^\circ_A + (p^\circ_B - p^\circ_A)\, x_B \qquad \ldots(3{\cdot}6)$$

This behaviour where $p^\circ_A > p^\circ_B$ is shown in Fig. 3.3.

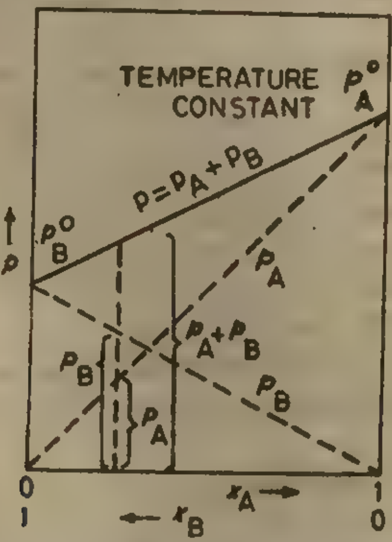


Fig. 3.3. Graph of vapour pressure against mole fraction (composition) for ideal solutions of two liquids A and B.

Figure 3·3 is a graph of the partial vapour pressure of each component against composition at constant temperature. The total vapour pressure of the solution is the sum of the partial pressures of the two components, *i.e.*, $p_A + p_B$, and always lies between that of pure A (p°_A) and pure (p°_B).

Essential requirements for forming an ideal solution

For the components of an ideal solutions, say liquids A and B, the forces of attraction and repulsion between molecules of A and B in the solution should be similar to those between molecules of A and A and between molecules of B and B Besides in the formation of an ideal solution ,the molecules of A and B must have equal volumes. As a result, (*i*) no heating or cooling is observed during the formation of ideal solutions, and (*ii*) no change in volume takes place during the mixing of its components :

Examples of ideal binary solutions are : (*i*) benzene-toluene, (*ii*) *n*-hexane, n-heptane, (*iii*) ethyl bromide-ethyl-iodide, (*iv*) chlorobenzene-bromobenzene, *etc*.

Exercise 3.3. *Toluene* (*p 139* mm Hg *at 333* K) *and benzene* (*p 392* mm Hg *at 333* K) *form an ideal solution.*

If in a solution the mole fraction of toluene is 0.60, what will be (*i*) *the partial pressure of each component,* (*ii*) *the total vapour*

pressure of the solution, and (c) the mole fraction of toluene in the vapour phase.

Solution. (*i*) If A represents benzene and B represents toluene, we have,

$$p_A = x_A p^\circ_A$$

$$p_B = x_B p^\circ_B$$

Now, $p_B = 0.600\ (139\ \text{mm Hg})$

$= 83.4$ mm Hg (partial vapour pressure of toluene)

$p_A = x_A p^\circ_A$

$= (1.00 - 0.60)(392\ \text{mm Hg})$

$= 157$ partial vapour pressure of benzene

(*ii*) The total vapour pressure of the solution is

$p_{total} = p_A + p_B$

$= (157 + 83.4)$ mm Hg

$= 240.4$ mm Hg

(*iii*) If y represents mole fraction in the vapour phase and p_{total} the total pressure, we can write

$p_A = y_A\ p_{total}$ $\qquad$ $p_B = y_B\ p_{total}$

or $\quad y_A = \dfrac{p_A}{p_{total}}$ $\qquad$ $p_B y_B = \dfrac{p_B}{p_{total}}$

$= \dfrac{157\ \text{mm Hg}}{240\ \text{mm Hg}}$ $\qquad$ $= \dfrac{83.4\ \text{mm Hg}}{240\ \text{mm Hg}}$

$= 0.654$ $\qquad$ $= 0.348$

(vapour phase mole fraction of toluene) $\qquad$ (vapour phase mole fraction of benzene)

(*ii*) **Non-ideal solutions** : If the two conditions discussed above are not fulfilled by the two liquids A and B, they form non-ideal solutions. Such solutions show either **positive or negative deviation** from Raoult's law. The intermolecular forces in these solutions will not be the same.

Positive deviation. If the attraction between the different molecules (A—B attraction) is weaker than between similar molecules (*i.e.*, A—A and B—B), the escaping tendency at the surface of the solution will be more than from the pure liquids. The system exhibits a maximum in the total vapour pressure curve (Fig 3.4). Such a system will exhibit positive deviation from Raoult's law. Examples are ethyl alcohol-chloroform, acetone-carbon disulphide (Fig. 3.5) benzene-cyclohexane and heptane-ethanol.

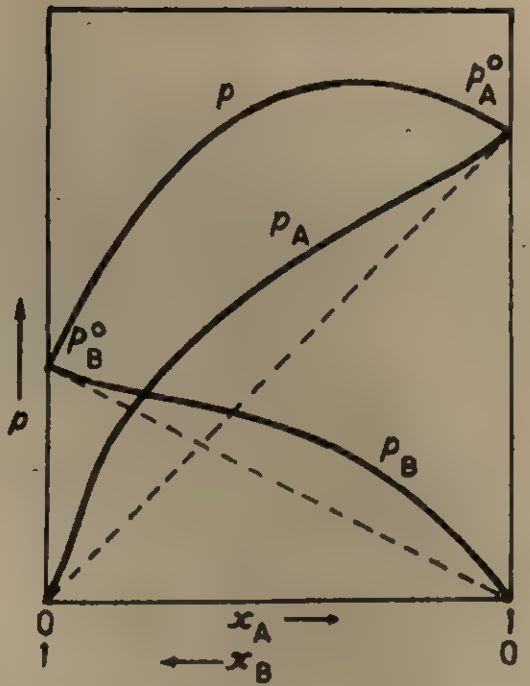


Fig. 3,4. Vapour pressure curves for a non-ideal solution showing positive deviation from Raoult's law (dotted lines show ideal behaviour).

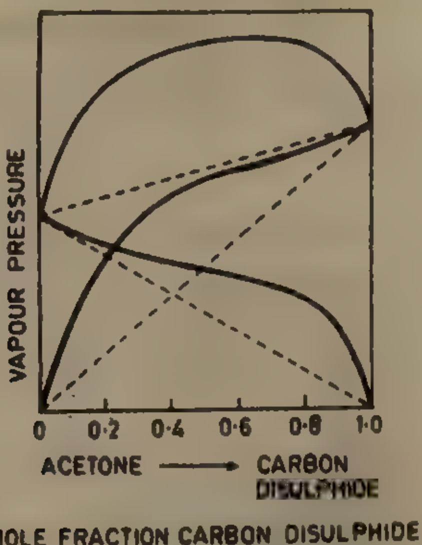


Fig. 3.5. Partial and total pressure curves for acetone-carbon disulphide system.

Negative deviation. On the other hand, if the attraction between the different molecules (A—B attraction) is greater than between similar molecules (*i.e.*, A—A and B—B) the escaping tendency at the surface of the solution will be less than from the pure liquids. The system exhibits a minimum in the total vapour pressure curve (Fig. 3.6). Such a system will exhibit negative deviation from Raoult's law. Examples are water-hydrochloric acid, chloroform-acetone (Fig. 3.7), and pyridine-acetic acid.

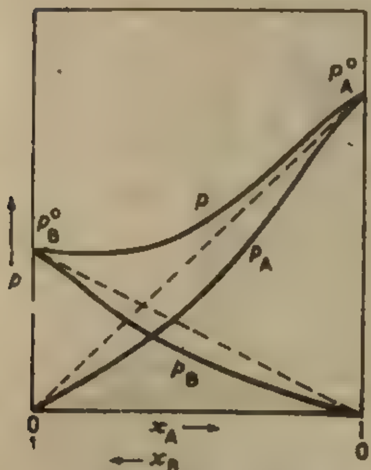


Fig. 3.6. Vapour pressure curves for a non-ideal solution showing negative deviation from Raoult's law (dotted lines show ideal behaviour).

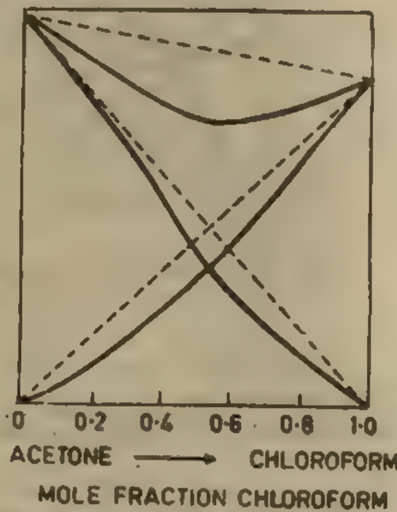


Fig. 3.7. Partial and total pressure curves for acetone-chloroform system.

3.5.3. Solutions of Solids in Liquids

Solids show a wide range of solubility in a liquid depending upon the nature and also on the type of interactions between solute and solvent. In order for a solid to dissolve in liquid, the attractive forces between the liquid and solid particles must be as great as the attraction between the molecules of the liquid and between the solid particles in the crystal.

When sugar dissolves in water, the hydrogen bonds between the C-OH groups of the sugar molecules are replaced by hydrogen bonds between these C-OH groups and water molecules. When iodine is dissolved in CCl_4, the London forces present between iodine molecules are replaced by London forces between iodine and CCl_4 molecules.

On the other hand, sugar does not dissolve in CCl_4 because the attraction of sugar molecules by CCl_4 will not supply enough energy to break the hydrogen bonds between sugar molecules. Similarly iodine does not dissolve in water as the dissolution process would not supply enough energy to dissociate the hydrogen bond-attractions between molecules. Here also the general principle of 'like dissolves like' is applicable.

Ionic solids dissolve only in very polar liquids. The solution process in water (polar) involves the formation of hydrated ions (Fig. 3.8).

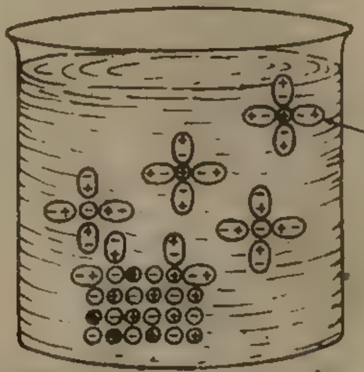


Fig. 3.8. Ions are attracted from the crystal lattice by the dipoles of H_2O

Solids and liquids are condensed states and are not very compressible. Therefore, the effect of pressure on the solubility equilibrium of a solution is negligible. The effect of temperature changes on the solubility of solids in liquids, however, is significant Further it depends on whether the dissolution process has an exothermic or endothermic nature.

An increase in temperature results in greater solubility for most substances (Fig. 3.9). At higher temperature a system becomes more random. A disordered condition is more favourable to any change. For exothermic dissolution, solubility decreases with increase in temperature whereas for endothermic dissolution, it increases with increase in temperature.

Properties of solutions of solids in liquids

The properties of a pure liquid are affected by the addition of a solid to form a solution. The major difference between the properties of the solution and those of the pure liquid is generally caused by the number of solute particles present in the solution. These properties of solutions, which are independent of the nature of the dissolved particles but depend upon the number of solute

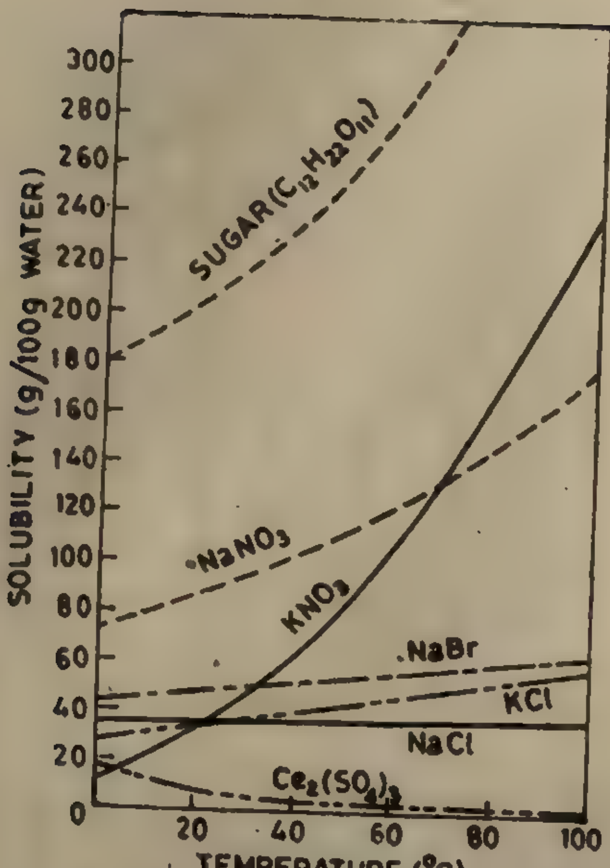


Fig. 3.9. The solubility of some solids in water as a function of temperature

particles are termed **colligative properties** (from the Latin word colligatus, "collected") and include the vapour pressure, boiling point, freezing point and osmatic pressure of the solution

If a binary solution is obtained by dissolving W_A g of the solvent of molecular mass M_A, and W_B g of solute of molecular mass M_B, then mole fraction of solute

$$x_B = \frac{W_B/M_B}{W_A/M_B + W_B/M_B}$$

or,

$$x_B = \frac{n_B}{n_A + n_B}$$

where n_A and n_B denote the amount of A and B respectively. Since $n_A \gg n_B$, for a dilute solution n_B can be neglected in the denominator. Therefore,

$$x_B \approx \frac{n_B}{n_A} \text{ for dilute solutions}$$

or,

$$x_B = \frac{W_B}{M_B} \times \frac{M_A}{W_A} \quad \ldots(3.7)$$

Since colligative property is proportional to the mole fraction of the solute, therefore,

$$\text{Colligative property} = Kx_B \quad \ldots(3.8)$$

where K is the proportionality constant which depends on the nature of the solvent only. Substituting the natue of x_B in (3·8), we get

$$\text{Colligative property} = K\frac{W_B}{M_A} \times \frac{M_A}{M_B} \quad \ldots(3.9)$$

If m denotes the molality of the solute in the solution, then

$$x_B = \frac{m}{m + \frac{1000}{M_A}}$$

Since $m \ll 1000/M_A$ in dilute solutions, we have

$$x_B = m\,\frac{M_A}{1000}$$

i.e., $x_B \propto m$ ...(3.10)

From equations (3.7) and (3.10), we get,

Colligative property $\propto x_B$

or Colligative property $= Km$ ...(3·11)

Equation (3.11) relates the colligative property to the molality of the solute in the solution. The proportionality constant, K *depends only upon the nature of the solvent, and can be defined as equal to the value of the colligative property for a one molal solution of the solute.*

(*i*) Vapour pressure

The presence of a non-volatile solute (such as glucose, sodium chloride) in a solvent lowers the equilibrium vapour pressure of the pure solvent.

This effect can be demonstrated dramatically (Fig. 3·10). Two open vessels, one containing pure solvent (water) and the other containing a solution (sugar+water) upto the same level are placed inside a sealed enclosure at room temperature. After a period of time it is observed that the level of pure water is lowered, while the level of

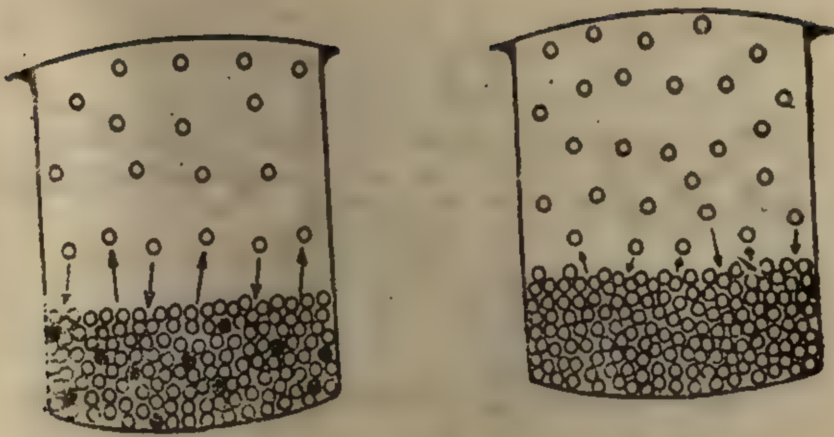
sugar solution is increased. This happens because through the process of evaporation and condensation water is transferred from the vessel containing pure water to the vessel containing sugar solution. This has been possible because the vapour pressure of pure water is higher than the vapour pressure of water in solution.

Fig. 3.10. A demonstration of the difference in vapour pressure between pure water and an aqueous sugar solution.

A simple explanation of why this happens is illustrated in Fig. 3.11. A non-volatile solute distributes itself throughout a solution, and some of the particles will be present at the surface [Fig. 11 (*a*)]. As a result, there will be fewer liquid molecules at the surface of the solution than at the surface of the pure liquid [Fig 3.11 (*b*)]. Thus, fewer of the solvent molecules can escape to the vapour phase. This is true at all temperatures. For a solution to have the same equilibrium pressure as the pure liquid it is necessary to increase the temperature. Increase in temperature increases the average kinetic energy of the molecules at the surface of the solution and therefore the number of solvent molecules at the surface.

It is thus obvious that solutions with larger concentrations of non-volatile solute particles have fewer solvent molecules at the surface. As a result, fewer molecules of solvent escape into the vapour phase. Now it can be predicted from this discussion that the more the solute particles present, the greater the effect of vapour pressure lowering.

The extent of lowering of vapour pressure thus depends upon the concentration of the non-volatile solute. According to Raoult's law, **the vapour pressure of the solution of non-volatile**



(*a*) (*b*)

Fig. 3.11. (a) The presence of solute particles at the surface reduces the number of solvent molecules able to escape into the vapour phase.

(b) The vapour pressure of a pure solvent is greater than that of a solution.

solute is equal *to the vapour pressure of the pure solvent,* **at the same** *temperature, times the mole fraction of the solvent in the solution.*

We know, Raoult's law holds good for ideal solutions. Ideal behaviour is not generally observed over a wide range of concentrations, but in dilute solutions of non-volatile solutes Raoult's law is mostly followed.

According to Raoult's law, $p_A = p^0_A x_A$ and $p^0_A - p_A$ is lowering in vapour pressure. Therefore,

$$p^0_A - p_A = p^0_A - p^0_A x_A$$

$$= p_A^0 (1 - x_A) \qquad \text{(Since } x_A + x_B = 1)$$

$$= p^0_A x_B$$

and

$$\frac{p^0_A - p_A}{p^0_A} = x_B$$

where

$$\frac{p_{0A} - P_A}{P^0_A}$$

is known as **relating lowering of vapour pressure**; x_B is the mole fraction of solute in the solution. The above equation can be used to determine molecular masses. The above equation can be written as :

$$\frac{p^0_A - p_A}{p^0_A} = x_B = \frac{n_B}{n_A + n_B}$$

$$= \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}+\frac{W_B}{M_B}}$$

where n_B and n_A are the amount of solute and solvent respectively.

W_A and W_B are the weights and M_A and M_B are the molecular masses of components A and B, respectively. Thus,

$$\frac{p^0_A - p_A}{p^0_A} = x_B = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}+\frac{W_B}{M_B}} \qquad \ldots(3.12)$$

In dilute solution, $\frac{W_B}{M_B}$, the amount of solute, is negligible compared to $\frac{W_A}{M_A}$, the amount of solvent. The term $\frac{W_B}{M_B}$ can thus be dropped from the denominator. We now get,

$$\frac{p^0_A - p_A}{p^0_A} = \frac{W_B}{W_B} \times \frac{M_A}{W_A} \qquad \ldots(3.13)$$

The above expression can be used to determine the molecular mass of the solute B for a solution of known concentration if we measure the relative lowering of vapour pressure and also know the molecular mass of A.

Exercise 3.4. *The vapour pressure of water at 293K is 17.0* mm Hg. *Calculate the vapour pressure of a solution having 3g of urea in 50g of water. Molecular mass of water is 18 and that of urea is 60.*

Solution. Amount of water $= \frac{50}{18} = 2.78$ mol

Amount of urea $= \frac{3}{60} = 0.05$ mol

$$x_{water} = \frac{2.78}{2.78+0.05} = \frac{278}{283}$$

$$p = p^0 x_{water}$$

$$p = 17{\cdot}0 \times \frac{278}{283} = 16.70 \text{ mm Hg}$$

(*ii*) Elevation of boiling point

The boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure. The vapour pressure of a solvent reduces on addition of a non-volatile solute. Thus, to make vapour pressure equal to atmos-

pheric pressure, we will have to heat the solution to a higher temperature. In other words, the boilimg point of a solvent is always raised by the presence of a non-volatile solute or the solution boils at a higher temperature than the pure solvent. The greater the amount of solute dissolved, the greater will be the lowering of vapour pressure, and hence the higher will be the boiling point.

In Fig. 3.12, AB depicts the variation of vapour pressure as a function of absolute temperature for a pure solvent, *e.g.*, water, and CD is the vapour pressure curve for solution of a non-volatile solute at different temperatures.

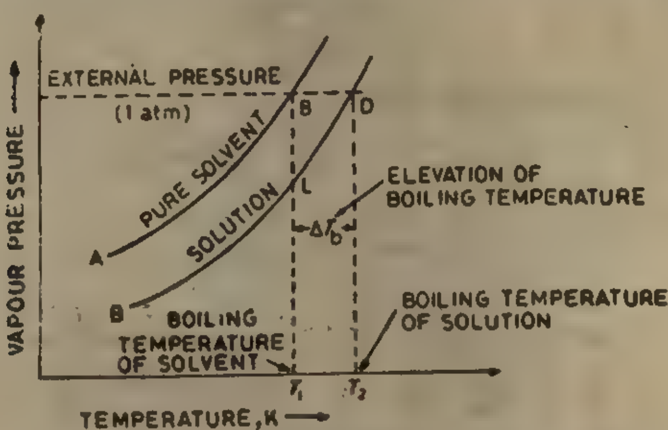


Fig. 3.12. Vapour pressure curves of a pure solvent and a solution of non-volatile solute (elevation of boiling point of a solution).

By drawing a constant pressure line at a pressure equal to the external pressure of one atmosphere we can determine the boiling points of solution and pure solvent. It is evident that the vapour pressure of the solution is lower than that of the solvent at all temperatures. At temperature T_1, the vapour pressure of the pure solvent (shown by B) becomes equal to the atmospheric pressure. Thus T_1 is the boiling point of the solvent. The vapour pressure of the solution at T_1 is much less as shown by point L in the figure. The vapour pressure in this case becomes equal to the atmospheric pressure (point D) only when the temperature is raised to T_2. Thus T_2 is the boiling point of the solution. The solution, therefore, boils at a temperature higher than that of the pure solvent. Evidently, the difference between the boiling point of the solution and of the pure solvent is known as the elevation of boiling point, ΔT_b.

$$\Delta T_b \propto p^\circ_A - p_A \qquad ...(3{\cdot}14)$$

Since the magnitude of ΔT_b is determined by that of the vapour pressure lowering, ΔT_b is also proportional to the solute concentration. Thus

$$\Delta T_b \propto x_B$$

or $$\Delta T_b = k_b x_B \qquad ...(3.15)$$

where k_b is the proportionality constant.

From equation (3.12)

$$x_B = \frac{\dfrac{W_B}{M_B}}{\dfrac{W_B}{M_B}+\dfrac{W_A}{M_A}}$$

Since the solution is dilute,

$$\frac{W_B}{M_B}+\frac{W_A}{M_A} \simeq \frac{W_A}{M_A}$$

$$x_B = \frac{\dfrac{W_B}{M_B}}{\dfrac{W_A}{M_A}} \qquad ...(3.16)$$

Substituting equation (3.16) in equation (3.15), we get

$$\Delta T_b = k_b \frac{W_B}{M_B}\,\frac{M_A}{W_A} \quad \text{or} \quad \Delta T_b = k_b\, M_A \frac{W_B}{M_B}\,\frac{1}{W_A}$$

or $$\Delta T_b = k_b \frac{M_A}{1000} \times \left[\frac{1000\ W_B}{W_A\ M_B}\right] \qquad ...(3.17)$$

If we take the mass of solvent, W_A, in kg, the term $\left[\dfrac{1000}{W_A}\,\dfrac{W_B}{M_B}\right]$ becomes molality, m of the solution (molality is the number of moles of the solute per kg of solvent). Thus,

$$\Delta T_b = \frac{k_b M_A}{1000} m$$

or $\Delta T_b = k_b\ m,$ ...(3.18)

where $k_b = \dfrac{KM_A}{1000}$

If $m = 1$, then, $\Delta T_b = k_b$ ...(3.19)

where k_b is the new proportionality constant and is called the **molal boiling point elevation constant** for the solvent. It may be defined as the elevation in boiling point of a solution containing 1 mole of a solute per kilogram of the solvent. Different solvents have their characteristic k_b values. In Table 3.3, k_b values (expressed as degree/molality, *i.e.*, K/m) of some solvents are given.

TABLE 3·3. Molal boiling point elevation constants for some solvents

Solvent	*Boiling point* (K)	K_b (K/m)
Acetic acid	391.3	3.07
Benzene	353.3	2.53
Carbon disulphide	319.4	2.34
Carbon tetrachloride	350.0	5.03
Chloroform	334.4	2.79
Cyclohexane	354·0	3.63
Ether	307.8	2.02
Ethyl alcohol	351.5	1.20
Water	373·0	0.52

Exercise 3.5. *A solution containing 2 g of a non-volatile solute in 100g of water boils at 373·03* K. *Find the molecular mass of solute* (K_b *for water*=0.52 K/m).

Solution. The boiling point elevation is,

$$\Delta T_b = 373.03 - 373 = 0.03 \text{ K}$$

$$K_b = 0.52 \text{ K}/m$$

If M_B is the molecular mass of the solute, then molality,

$$m = \frac{2}{M_B}\,\frac{1000}{100}$$

Now $\Delta T_b = K_b m$

Substituting the values of m, K_b and ΔT_B

$$0.03 = 0{\cdot}52 \times \frac{2}{M_B}\,\frac{1000}{100}$$

$$M_B = \frac{0.52 \times 2 \times 10}{0.03} = 346.7 \text{ g mol}^{-1}$$

(*iii*) **Depression in freezing point**

The freezing point of a substance is the temperature at which the vapour pressure of the liquid and the solid phases of the substance are the same. It has been found that if a non-volatile solute is dissolved in a solvent the freezing point of the solution is lowered down as shown in Fig. 3.13. Upon freezing, the solid phase present in equilibrium with the dilute solution, consists of pure

solvent. Thus, by drawing vapour pressure-temperature curve near the freezing point for the solid solvent, pure liquid solvent, and the solution (Fig. 3.13), the freezing temperature can be found out as the temperature at which the liquid curve cuts the solid curve.

In Fig. 3.13, AB is the sublimation curve of the solid solvent and BC is the vapour pressure curve of the pure liquid solvent. The freezing point of the pure solvent is T_1 corresponding to the point B. At this point B the liquid and solid state are in equilibrium with each other and have identical vapour pressures. DE is the vapour pressure curve of the solution.

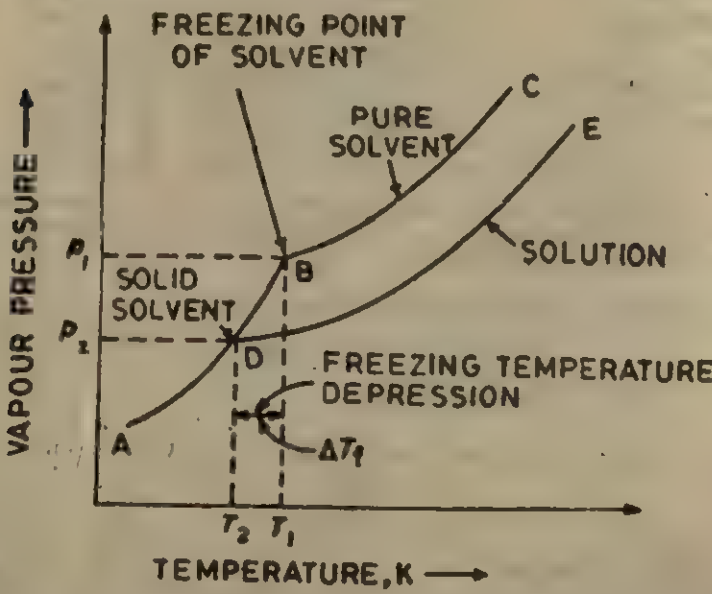


Fig. 3.13. Vapour pressure versus temperature near the freezing point for pure solvent, solid solvent and a solution of non-volatile solute (depression of freezing point of a solution).

Since vapour pressure of a solution is always less than the vapour pressure of the pure solvent, the solution curve will meet the sublimation curve (vapour pressure curve of solid solvent) at lower temperature, and hence, the freezing point of the solution will be always lower than the freezing point of the pure solvent as shown in Fig. 3.13. Since lowering of vapour pressure is proportional to the mole fraction of solute, the lowering of freezing point is also proportional to the mole fraction of the solute.

$$\Delta T_f \propto \Delta p \propto x_B$$

or

$$\Delta T_f = k_f \times x_B \qquad ...(3.20)$$

For dilute solutions,

$$\Delta T_f = k_f \frac{W_B}{M_A} \times \frac{M_A}{M_B}$$

or

$$\Delta T_f = KM_A \frac{W_B}{W_B} \cdot \frac{1}{W_A}$$

or

$$\Delta T_f = \frac{KM_A}{1000} \left[\frac{1000\ W_B}{W_A\ M_B} \right] \quad ...(3.21)$$

If we take the mass of the solvent W_A in *kg*, the term $\left[\frac{1000\ W_B}{W_A M_B} \right]$ becomes molality *m* of the solution. Thus,

$$\Delta T_f = \frac{KM_A}{1000} m$$

or $\Delta T_f = K_f m$, ...(3.22)

where $K_f = \frac{KM_A}{1000}$

if $m=1$, then, $\Delta T_f = K_f$ ...(3.23)

where K_f is the **molal freezing point depression constant or molal cryoscopic constant** for the solvent. It is defined as the depression in freezing point of a solution containing 1 mole of a solute per kilogram of the solvent. Each solvent possesses a characteristic value of K_f. Table 3.4 lists K_f values for some solvents.

TABLE 3.4. Molal freezing point depression constant for some solvents

Solvent	*Freezing point* (K)	K_f (K/*m*)
Acetic acid	289.7	3.90
Benzene	278.6	5.12
Camphor	452.0	39.70
Carbon disulphide	164.2	3.83
Carbon tetrachloride	250.5	31.80
Chloroform	209.7	4.70
Cyclohexane	279.5	20.20
Ether	156.9	1.79
Ethyl alcohol	155.7	1.99
Naphthalene	353.3	6.80
Water	273.0	1.86

Exercise 3.6. *Find the freezing point of a solution containing 9 g glucose ($C_6H_{12}O_6$) dissolved in 100 g water (K_f for water = 1.86* K *m*)

Solution : Molecular mass of glucose, $M_B = 180$

$$\text{Molality, } m = \frac{9}{180} \cdot \frac{1000}{100}$$

$$K_f = 1.86 \text{ K}/m$$

The freezing point depression is,

$$\Delta T_f = K_f\, m$$

$$= \frac{1.86 \times 9 \times 1000}{180 \times 100} = 0.93\text{K}$$

The freezing point of the solution is

$$273\text{K} - 0.93\text{K} = 272.07\ \text{K}$$

Exercise. 3·7. *A solution of 2 g of non-volatile solute in 20 g of water freezes at 271 K. Calculate the molecular mass of solute. The molal depression constant, $K_f = 1.86\ \text{Km}^{-1}$.*

Solution. If ΔT_f denotes the depression in freezing point produced in solution of molality, m, with respcct to the solute, then we have

$$\Delta T_f = K_f\, m \qquad ...(i)$$

Let M be the molecular mass of the solute, then

$$m = \frac{2/M}{20} \times 1000$$

or

$$m = \frac{2}{20M} \times 1000 = \frac{100}{M} \text{ moles per thousand g of the solute}$$

$$K_f = 1\cdot86\ \text{K mol}^{-1}$$

Assuming the freezing point of pure water to be 273 K

ΔT_f = freezing point of pure water − freezing point of the solution

$$= 273 - 271 = 2\ \text{K}$$

Substituting these values in the equation $\Delta T_f = K_f\, m$, we get,

$$2\ \text{K} = \frac{1\cdot86\ \text{K mol}^{-1} \times 100\ \text{mol}}{M}$$

or

$$2 = 1.86 \times \frac{100}{M}$$

$$M = \frac{1\cdot86 \times 100}{2} = 93\ \text{g mol}^{-1}.$$

(iv) Osmotic pressure

It has been seen earlier (Fig. 3.10) that the rate of vaporization of the pure liquid is greater than that from the solution. As a result, there is a net transfer of solvent from the pure liquid to the solution as the equilibrium between the vapour and the pure liquid and that between the vapour and the solution is established.

A similar transfer of solvent, '**osmosis**' from a less concentrated to a more concentrated solution occurs through a variety of membranes parchment, various synthetic films such as cellophane and

biological membranes—known as semipermeable membranes. A semipermeable membrane permits the passage of solvent and some ionic solutes but not the larger solute molecules to pass through it. As seen earlier (Fig. 3.10), the transfer of solvent through the membrane takes place at a faster rate from the less concentrated solution or from pure solvent [Fig. 3.14 (*a*)]. The solute interferes with the passage of solvent molecules in the same way as the solute reduces the rate of evaporation from the solution.

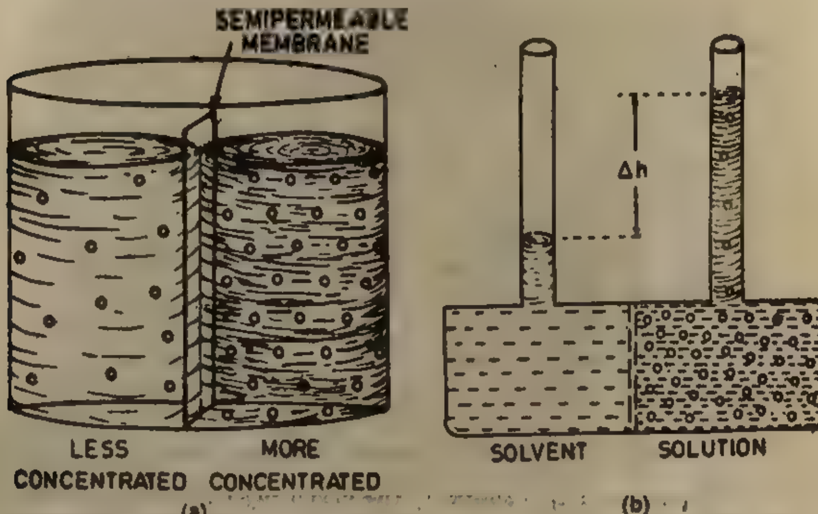


Fig. 3.14. (a) Osmosis is a transfer of solvent molecules from a less concentrated to a more concentrated solution.

Fig. 3.14. (b) The penetration of solvent molecules genetrates a pressure which causes the column of the solution to rise above the level of the pure solvent by the amount Δh.

In an apparatus planned as in Fig. 3.14 (*b*), the penetration of solvent into the solution compartment causes the level of the solution to rise in the capillary. This penetration is continued till the hydrostatic pressure created on the solution side becomes equal to the difference of the tendencies of the solvent to pass through the membrane. Thus the transfer of solvent into the solution produces a hydrostatic pressure, known as **osmotic pressure**, proportional to the difference in height Δh between the two columns of liquid [Fig. 3.14 (*b*)].

The passage of solvent from pure solvent compartment to solution compartment can also be prevented by either increasing external pressure on the solution or decreasing external pressure on the solvent by a factor equal to the osmotic pressure (π) (Fig. 3.15).

The excess pressue which must be applied to the solution in order to prevent the flow of solvent molecules into the solution through semipermeable membrane separating the solution from pure solvent is termed as **osmotic pressure.**

"The osmotic pressure of a solution is the excess pressure which must be applied so that the vapour pressure of the solution becomes equal to that of the pure solvent."

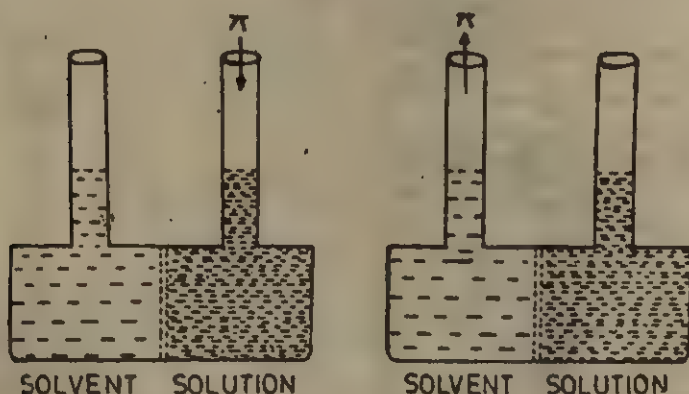


Fig. 3.15. Arrangement for stopping osmosis.

"The osmotic pressure of the given solution can also be defined as the negative pressure or the pressure withdrawn externally from the pure solvent in order to decrease its vapour pressure until it becomes equal to that of the solution."

Dependence of osmotic pressure on concentration and temperature

Van't Hoff after studying large amount of data on osmotic pressure of the same solution at different temperatures, and of solutions of different concentrations with respect to the solute at the same temperature, enunciated the following laws :

Van't Hoff-Boyle's law states that at a constant temperature the osmotic pressure of the given solution is directly proportional to the concentration of the solute expressed in molarity as,

$$\pi \propto C$$

$$= A(T)\, C \qquad ...(3{\cdot}24)$$

where π is the osmotic pressure of the solution, C molar concentration of the solute at temperature T. $A(T)$ is the proportionality

constant which is a function of temperature only. If n is the amount of moles of the solute present in V dm^3 of the solution, then

$$C=\frac{n}{V} \qquad \ldots(3.25)$$

Substituting the value of C from (3.25) in (3.24), we get

$$\pi \propto \frac{n}{V} \qquad (T=\text{const})$$

i.e., **osmotic pressure of a given solution containing n moles of the solute is inversely proportional to the volume of the solution at a constant temperature.** The product of osmotic pressure and volume of the solution is constant. This is Van't Hoff's first law and is the analogue of Boyle's law of gases.

Similarly, Van't Hoff found that the analogue of Charles' law for solutions can be stated as :

Osmotic pressure of a given solution of fixed concentration is directly proportional to the absolute temperature. This is known as pressure temperature law for dilute solutions.

$$\pi \propto T \qquad (C \text{ const.})$$

On combining these two laws, the general equation for state of dilute solutions can be deduced, which is similar to the equation of state for a perfect gas.

Since osmotic pressure at constant temperature,

$$\pi \propto \frac{1}{V} \qquad (n \text{ and } T \text{ const.}) \qquad \ldots(3.26)$$

and for a solution of [fixed composition (concentration) the osmotic pressure),

$$\pi \propto T \qquad \left(\frac{n}{V} \text{ const}\right)$$

By combining equations (3.26) and (3.27),

$$\pi \propto \frac{T}{V} \qquad (\text{if both } T \text{ and } V \text{ vary}) \ldots(3.27)$$

or $$\pi V=AT \qquad (n \text{ constant})$$

where, A, is the proportionality constant.

It has been found experimentally that, if $n\neq 1$, A is equal to nR, where R is the gas constant. The expression, therefore, becomes,

$$\pi V=n\,RT \qquad \ldots(3.28)$$

This expression has the same form as the equation of state for n mole of a perfect gas.

From equation 3.28,

$$\pi = \frac{n}{V} RT$$

$$= CRT \qquad \ldots(3.29)$$

This relationship suggests that the striking similarity between the theory of ideal gases and of ideal solutions. It is important to note that in a gas the molecules tend to occupy any available space, whereas in a solution the solute molecules occupy only the fixed volume of the solution. The solute molecules can be considered as experiencing the same kind of random motion in the solution as the gas molecules. Van't Hoff thus proposed that a substance in dilute solution can be regarded as behaving exactly as a gas. **The osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature, and occupying the same volume as that of the solution.**

It can be further deduced that like other colligative properties, osmotic pressure is also proportional to the mole fraction of the solute. If x_B denotes the mole fraction of the solute, then for a dilute solution,

$$x_B = \frac{n_B}{n_A}$$

Since, $C = \frac{n_B}{V}$

Therefore, $C = \frac{x_B \, n_A}{V}$

Substituting this value of C in equation (3.29),

$$\pi = x_B \times \frac{n_A}{V} \times RT$$

which means that at a constant temperature,

$$\pi \propto x_B$$

and, hence, osmotic pressure is a colligative property.

Exercise 3.8. *10 g of a non-volatile solute dissolved in one litre of water gave osmotic pressure of 1.18* atm *at 273* K. *Calculate the molecular mass of the solute.*

Solution. From equation,

$$\pi = CRT = \frac{n}{V}\ RT$$

If M_B is the molecular mass of the solute, then,

$$1.18 = \frac{10/M_B}{1} \times 0.0821 \times 273$$

or
$$M_B = \frac{10 \times 0.0821 \times 273}{1.18}$$

$$= 190 \text{ g mol}^{-1}$$

Measurement of Osmotic Pressure

Osmotic pressure is usually measured by the method of Berkley and Hartley. It consists in measuring the external or counter pressure applied to the solution mechanically which is just sufficient to prevent the entry of the solvent into solution. This corresponds to the osmotic pressure of the solution.

The apparatus consists of a strong vessel into which a porous tube is fitted (Fig. 3.16). The inner walls of the tube are covered with a strong semipermeable membrane consisting of a film of copper ferrocyanide, $Cu_2[Fe(CN)_6]$. The tube is mounted inside a metallic cylinder with air tight joints. The porous tube A is filled with pure water and the cylinder contains solution whose osmotic pressure is to be determined.

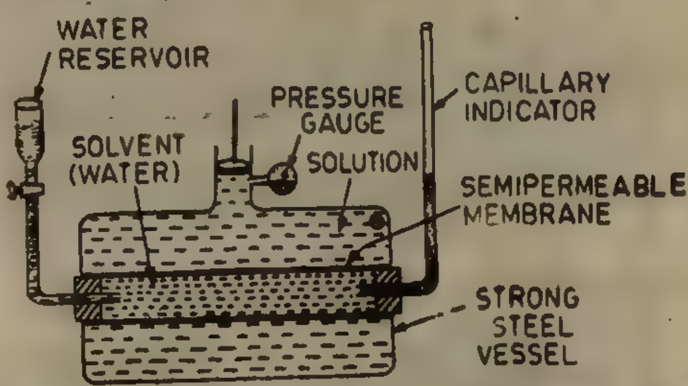


Fig. 3.16. Determination of osmotic pressure (Berkley and Hartley method).

Due to osmosis, water tends to flow from the porous tube into the solution through the membrane. It is shown by the fall in water level in the capillary indicator. This flow or osmosis of water into the solution can be stopped by the application of external pressure on the solution with the help of a piston and the level in the capillary tube is maintained. The pressure so applied is equal to the osmotic pressure and is indicated by the pressure gauge.

The phenomenon of osmosis is used in producing fresh water from the oceans. If salt water is pumped under pressure into a tank fitted with a semipermeable membrane, water molecules will pass through the membrane, leaving the ions behind (Fig. 3.17). In this operation, water moves across the membrane from more concentrated side to less concentrated side because of the high pressure applied to the salt-water side. This process is referred to as **reverse osmosis.**

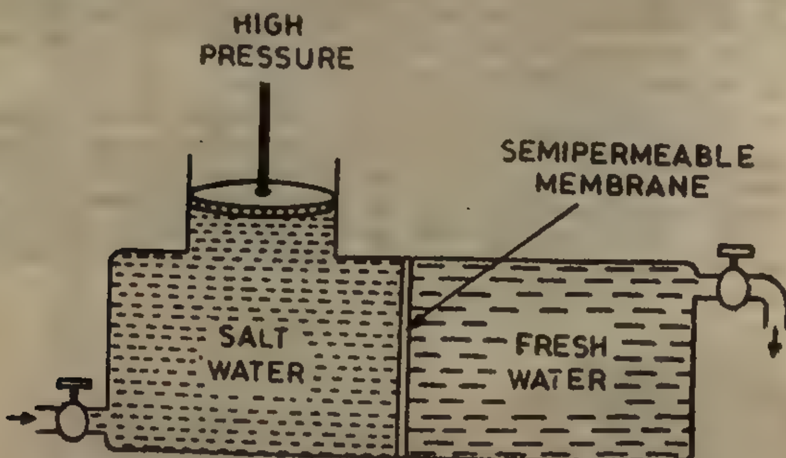


Fig. 3.17. A schematic representation of the desalinisation of water by reverse osmosis.

3·6 MOLECULAR MASS DETERMINATION

Molecular masses of gases and volatile liquids can be determined from gas density data. But this cannot be applied to non-volatile solids. Measurement of colligative properties offers us methods to determine the molecular masses of non-volatile substances, dissolved in volatile solvent. Measurements of lowering of

vapour pressure and of osmotic pressure have the advantage that these can be measured at any temperature. On the other hand, the depression of freezing point, and the elevation of boiling point measurements can be done only at the freezing point or boiling point of the solvent. More precise results are obtained from freezing point depression than from boiling point elevations since the molal depression constant (K_f) is always larger than the molal elevation constant (K_b) which produces larger values of $\triangle T$. Further fluctuations in atmospheric pressure do not affect freezing points as are boiling points. But elevation of boiling point method has the advantage that at the boiling temperature of the solvent, the solubility is much higher than the solubility at the freezing temperature.

Osmotic pressure measurements serve best for determining the molar masses of very large molecules such as polymers, proteins and other macromolecules, because these substances are not very soluble and the number of the large molecules present in solution is small. The values of osmotic pressures for even very dilute solutions are very large, *e.g*, for 0.1 molar solution of the solute, the osmotic pressure at 298 K is of the order of 2.224 atmospheres.

Method of Determining Depression of Freezing point

With the help of Beckmann thermometer, it is possible to measure the relative changes in temperature in the presence and the absence of the solute very precisely (within $\pm 0.01°$).

In the Beckmann method of the measurement of $\triangle T_f$, the apparatus used is shown in Fig. 3.18. It consists of an outer tube, to provide an air column which allows the cooling to occur slowly. The procedure involves weighing of a known volume of the solvent (W_A) and freezing the solvent kept in the freezing point tube by cooling with a suitable freezing mixture as shown in Fig. 3.18. The freezing point on the thermometer is noted. The freezing bath is adjusted to a temperature slightly lower than the freezing point of the pure solvent. The temperature in the Beckmann thermometer is pre-set at the upper level. The solvent is melted by taking the freezing point tube out of the bath and a weighed quantity of W_B of the solute is added. The solution is stirred to obtain a homogeneous dilute solution. The solution is frozen again by immersing the tube in the freezing mixture and the temperature relative to the freezing point of the pure solvent is noted. The solution requires continuous stirring to prevent supercooling and cooling should be done slowly.

It may be mentioned here that although absolute value of the freezing point cannot be measured with the Beckmann thermometer, the lowering of freezing point or elevation of boiling point can be measured with a precisions of 0.01°.

Now using equation (3.22) molecular mass can be calculated.

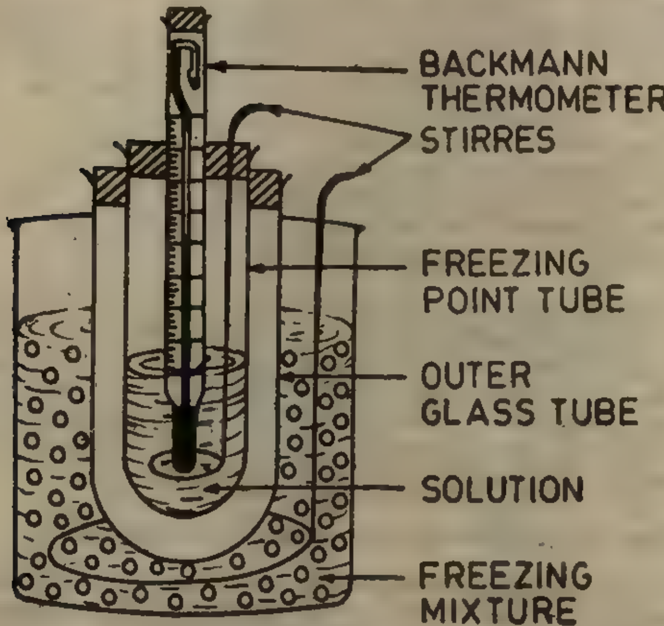


Fig. 3.18. An assembly for measurement of depression of freezing point.

Abnormal Molecular Masses

In this unit, we have seen that colligative properties depend on the number of molecules of the solutes in the solution. Solutions like those of salts in water or of benzoic acid in benzene give colligative properties which do not agree with normal values. These are called abnormal solutions. Such abnormalities may be due to (*i*) association of solute molecules, and (*ii*) dissociation of solute molecules.

Using equations given under colligative properties for solutes undergoing dissociation in the solution, the molecular masses obtained are much less than their normal values. This is because solutes dissociate into ions in solvents, and thus, produce lower vapour pressure, a higher boiling point, a lower freezing point and a greater osmotic pressure than their normal values.

Some solutes like acetic and benzoic acids undergo association in solution. Their molecular masses were found to be just their normal values. Association leads to a decrease in the of molecular particles in the solution. Both acetic and acids exist as dimers of the type $(CH_3COOH)_2$ and OH)$_2$ respectively.

In order to account for all abnormal cases, Van't Hoff introduced the factor, *i*, known as Van't Hoff's factor. It expresses the degree of association or dissociation and can be written as

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

In case of association, *i* is less than unity while it is more than unity in case of dissociation.

3.7 SOLID SOLUTIONS

A homogeneous distribution of a solute throughout a solid phase is a solid solution. Solid solutions of gases in solids and solids in solids are well-known. Figure 3.19(*a*) represents a solid solution of copper and zinc. Empty circles represent atoms of copper and black circles represent zinc atoms. The atoms in a solid solution are closely packed as in the case of a crystal. But there is no order as to which lattice points are occupied by which type of atoms. Many alloys are examples of solid solutions, *e.g.*, steel is a solid solution in which carbon atoms are distributed randomly in the spaces between iron atoms which are arranged in a regular pattern of pure iron. Some of the alloys are heterogeneous mixtures, *e.g.*, Bi-Cd alloy. Many alloys are formed, however, by chemical combination of metals resulting in the formation of intermetallic compounds, *e.g.*, $MgCu_2$. Palladium and hydrogen gas form solid solutions of solid and gas. Chlorobenzene (solid) and bromobenzene (solid) below their freezing point form completely homogeneous solid solutions. Generally, the common solid solutions are of two types :

In **substitutional solid solutions**, an atom or ion of similar electronegativity and size as the host (solvent) replaces host atoms or ions in the crystal lattice [Fig. 3.19 (*a*)]. The properties of the such solid solutions are different from those of pure metals, *e g.*, brass takes a high polish not possible with individual copper and zinc, solder melts at lower temperature than both lead and tin (alloying materials).

Interstitial solid solutions are obtained as a result of insertion of a small atom, such as carbon, boron, *etc.*, into the tetrahedral or octahedral holes in the close packed lattice of the host, *e.g.*, transition metals [Fig. 3.19 (*b*)]. Such solutions are hard, brittle and very high melting. Tungsten carbide is an example of interstitial solid solution. Hydrogen atoms occupy the lattice of palladium metal.

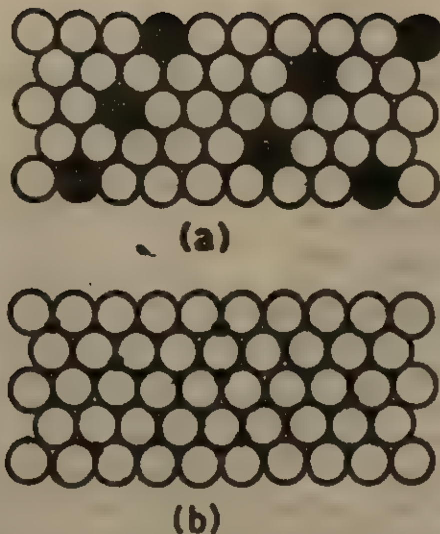


Fig. 3.19. Representation of solid solutions :
(a) substitutional solid solutions, and
(b) interstitial solid solutions.

3.8 ELECTROLYTE SOLUTIONS

A water solution prepared from an ionic solid contains more than 1 mole of particles for each mole of solute dissolved. For example, 1 mole of NaCl furnishes 2 moles of ions (Na^+ and Cl^-) ; 1 mole of $MgCl_2$ furnishes 3 moles of ions (Mg^{2+}, Cl^-, Cl^-). Such solutions are called electrolyte solutions [Fig. 3.20 (*a*)] because of their ability to conduct an electric current. The aqueous solutions of non-ionic solutes such as sugar are called non-electrolyte solutions as they do not conduct electric current [Fig. 3·20 (*b*)].

The dissolution process of electrolytes has already been discussed in Section 3·5·3. According to Arrhenius, the presence of ions that are free to move is essential for the conductance of electric current by a solution.

When the solute is an electrolyte, the formation of ions results in a higher concentration of particles than the concentration based on the number of moles of solute dissolved, and the quantitative application of colligative properties becomes complex. The molality of such solutions depend upon the number of ions. For example, the equilibrium concentration of undissociated HX is less than 1 molal,

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

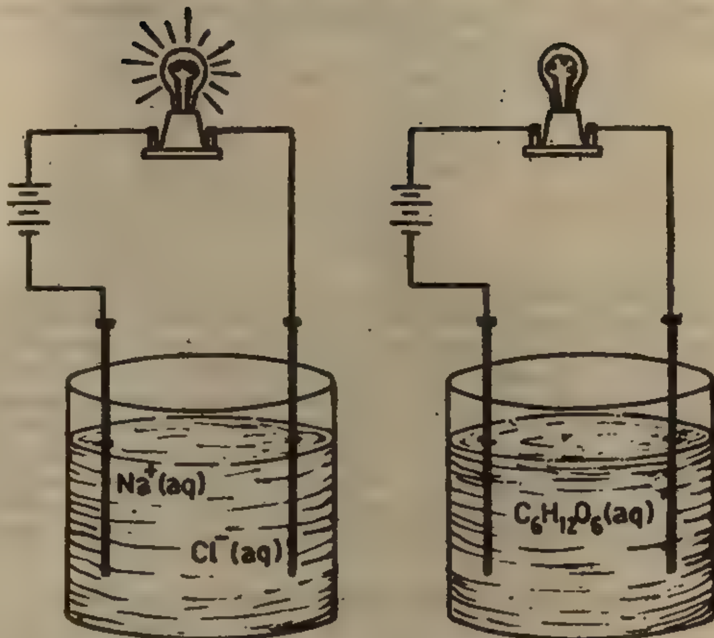


Fig. 3.20. Investigation of the conductivity of solutions :
(a) solutions of electrolytes conduct electric current
(b) solutions of non-electrolytes do not conduct electric current.

but for each molecule dissociated two ions are contributed. Since the concentration of solute particles is the sum of the concentration of HX, H_3O^+ and X^-, the molality of the particles is greater than one. As a result, the freezing point of this solution will be lowered, more than 1.86 °K and the boiling point will be raised more than 0.512 °K. Similarly the vapour pressure will be lowered by a factor larger than is predicted by Raoult's law; and the osmotic pressure will also be greater than is predicted.

According to Van't Hoff dilute solutions of electrolytes have osmotic pressure nearly two or three times those of non-electrolyte solutions of equal concentration.

Accordingly, Van't Hoff changed the osmotic pressure equation.

$$\pi = i\,CRT$$

or

$$i = \frac{\pi}{CRT}$$

where the i factor represents, in effect, the number of moles of ions per mole of solute. Similarly the other colligative properties can be modified to,

$$\Delta T_f = i\, K_f\, m$$

and

$$\Delta T_b = i\, K_b\, m$$

$$i = \frac{\Delta T_f}{K_f\, m}$$

$$i = \frac{\Delta T_b}{K_b\, m}$$

The expressions show that the colligative properties can be used to count the number of particles per mole of solute present in the solution, *i.e.*, to measure the value of i. For non-ionic solutes i has a value of 1. The calculated values of i on different concentrations of ionic solutes reveals that i is not a constant and that its values are smaller than the value to be expected for the number of moles of ions per mole of solute. It has been found that the value of i is more ideal in dilute solutions It has been suggested by Debye and Huckel that the deviations from ideality result from interaction between ions. The values of i for certain ionic solutes are given in Table 3·5.

TABLE 3·5. Variation of Van't Hoff factor with concentration

Solute	*Moles of ions per mole*	*i values*		
		0.1 m	*0.01* m	*0.001* m
NaCl	2	1.87	1.94	1.97
$MgSO_4$	2	1.21	1.53	1.82
K_2SO_4	3	2.32	2.69	2.84

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

3.1. Choose the correct answer out of the four alternatives given for the following questions :

(*i*) Which of the following statements is wrong ?

(*a*) Molarity of a solution depends upon temperature.

(*b*) Molality of a solution is independent of temperature.

(*c*) Mole fraction of a solution is dependent on temperature.

(*d*) Mole fraction of solute is proportional to the molality of the solution.

(*ii*) Which of the following is not a colligative property ?

(*a*) Freezing point depression

(*b*) Osmotic pressure

(*c*) The boiling point of the solvent

(*d*) Vapour pressure lowering

(*iii*) A 1 dm^3 quantity of 0.10 M solution of HCl contains

(*a*) 0.1 mol (*b*) 0.2 mol

(*c*) 1.0 mol (*d*) 10 mol.

(*iv*) What is the freezing point of a 0.100 m aqueous solution of a non-electrolyte ? For water $K_f = 1.86$

(*a*) 18.6°C (*b*) 0.186°C

(*c*) 1.86°C (*d*) −1.86°C.

(*v*) If a solution of each of the following have the same concentration, which has the lowest freezing point ?

(*a*) NaCl (*b*) CH_3OH

(*c*) CaS (*d*) Na_2SO_4.

(*vi*) Which of the following statements is wrong ?

(*a*) The constituents of an ideal solution follow Raoult's law under all conditions.

(*b*) The addition of non-volatile solute to a volatile solvent increases the boiling point of the latter.

(*c*) Henry's law deals with the variation of solubility of gas with temperature.

(*d*) The ideal behaviour of a liquid solution is due to the fact that the interactions between different molecules are of the same magnitude as the solute-solute and solvent-solvent interactions.

(*vii*) The presence of a non-volatile solute in a liquid causes a

(*a*) decrease in vapour pressure

(*b*) decrease in the boiling point.

(*c*) increase in the freezing point.

(*d*) increase in vapour pressure.

(*viii*) If p° and p are the vapour pressures of a solvent and its solution respectively, and x_A and x_B are the mole fractions of the solvent and the solute respectively then

(*a*) $p = p^\circ x_A$ (*b*) $p = p^\circ x_B$

(*c*) $p^\circ = p x_A$ (*d*) $p^\circ = p x_B$.

(*ix*) The Van't Hoff factor *i* for a dilute solution of $NaHSO_4$ is likely to be

(*a*) 1 (*b*) 2

(*c*) 3 (*d*) ½.

(*x*) If an elevation of freezing point is observed, we can conclude that

(*a*) a solid solution is formed.

(*b*) the solvent is a non-polar solvent a solid solution in which the solute is more soluble in the liquid phase is formed.

(*d*) a solid solution in which the solute is more soluble in the solid phase is formed.

3.1. **Fill in the blanks :**

(*i*) A solution that contains as much solute as can be dissolved at that temperature in the presence of undissolved solute is called.........

(*ii*) A ideal solution is one which obeys.........

(*iii*) The partial vapour pressure of a component in a solution is equal to the...............of that component times its vapour pressure when pure.

(*iv*) Properties of a solution which depend upon the...............of solute particles and not upon their identity are known as............... properties.

(*v*) A...............deviation from Raoult's law is one in which the partial vapour pressure of each component is...........than that in an ideal solution.

(*vi*) Molarity is the number of...............of solute dissolved............... of solution.

(*vii*) Molality is the number of...............of solute dissolved............... of solvent.

(*viii*) The solubility of a gas dissolved in a liquid is proportional to the ....of the gas above the liquid.

(*ix*) At each temperature the vapour pressure of a solution is............... as a result of the presence of a...............

(*x*) Osmotic pressure is directly proportional to the...............of the dilute solution and to the...............

3.3. **Choose the true (T) and false (F) statements of the following :**

(*i*) Osmosis is the process by which solvent molecules pass through a semipermeable membrane from a dilute solution into a more concentrated solution.

(*ii*) Mole fraction of a component in solution is the number of moles of the component divided by the sum of the number of moles of all components.

(*iii*) Colligative properties of solution depend upon the nature of solute particles present.

(*iv*) The vapour pressure of a solvent in solution decreases as its mole fraction decreases.

(*v*) The negative deviation from Raoult's law is caused by unusual strong repulsions between like molecules.

(*vi*) The molal boiling elevation constant of a solution depends upon the nature of solute.

(*vii*) For very dilute solutions, osmotic pressure (π) follow the equation $\pi = MRT$.

(*viii*) The molal freezing point depression constant, K_f is given by the equation.

$$K_f = \frac{\Delta T_f}{M}$$

(*ix*) The vapour pressure of a component in a solution is given by the expression $p_A = x_A\, p^\circ_A$.

(*x*) The concentration of a gas in a solution is proportional to the pressure of the gas above the surface of the solution.

SHORT ANSWER QUESTIONS

3.4. (*i*) Why will ice melt when placed in an aqueous solution at 0°C ?

(*ii*) Account for the presence of tremendous quantities of soluble substances in sea water.

(*iii*) How may the boiling point of liquid-liquid solution be defined ?

(*iv*) What determines whether the dissolving of a solid in a liquid will be an exothermic or an endothermic process ?

(*v*) Describe the effect of increasing the pressure on the solubility of gases in liquids.

(*vi*) Explain in your words why the vapour pressure of a solvent is lowered by dissolving a non-volatile solute in it.

(*vii*) Explain in your words why boiling points are elevated, whereas freezing points are depressed by dissolving non-volatile solutes in solvents.

(*viii*) What is the effect of electrolytes as compared to non-electrolytes on freezing point depression ?

(*ix*) What is the effect of ion association on freezing point depression ?

(*x*) What are osmosis and osmotic pressure ?

TERMINAL QUESTIONS

3.1 Explain the terms : (*i*) Solution, (*ii*) Solvent, and (*iii*) Solute. What are the various modes of expressing the concentration of a solution ?

3.2 Define : (*i*) unsaturated, (*ii*) saturated, and (*iii*) supersaturated solutions. Give an experiment to show that a solution is saturated, unsaturated or supersaturated.

3.3 Give the classification of solutions with appropriate examples.

3.4 What are ideal and non-ideal solutions ?

3.5 State and explain Raoult's law.

3.6 What are positive and negative deviations in case of non-ideal solutions ? Explain the causes of such deviations.

3.7 What are the colligative properties of solutions ? On what factor do these properties depend ?

3.8 Derive the relationship between elevation of a boiling point and molecular mass of a solute.

3.9 What is a colligative property ? Explain, how the vapour pressure of a solution of non-volatile solute is lower than the vapour pressure of the pure solvent ?

3.10 Explain why the boiling point of a solvent is elevated and its freezing point depressed by the addition of a solute ?

3.11 What is osmosis ? Describe an experiment to determine the osmotic pressure of a solution.

3.12 What is molal depression constant ? How will you determine the depression in freezing point experimentally.

3.13 Explain how various colligative properties change from their normal values when a solute in a solution undergoes (*i*) association, and (*ii*) dissociation.

3.14 How is molecular mass of a solute related to the depression in the freezing point ?

3.15 Explain the terms osmosis and osmotic pressure. How does osmosis differ from osmotic pressure ?

3.16 Write the expression for Van't Hoff's solution equation. Give the significance of each term involved.

3.17 **How do you explain :**

(a) if the vapour pressure of liquid A is greater than the vapour pressure of liquid B at room temperature, then the boiling point of liquid A is lower than the boiling point of liquid B.

(b) Vapour pressure of a solution containing non-volatile solute in a volatile solvent at a given temperature is lower than the vapour pressure of the pure solvent.

3.18 Definite relative lowering of vapour pressure, and show that it is equal to the mole fraction of the non-volatile solute in a dilute ideal solution.

3.19 Illustrate with examples different types of non-ideal solutions. Explain the reasons for positive and negative deviations from ideal behaviour.

3.20 What mass of barium chloride would be required to make 500 g of a 5% solution of that salt ? (**Ans.** 25 g)

3.21 Calculate the mass of solute required to make each of the following solutions :

(i) 750 mL of 2.5 M NaCl (**Ans.** 109.69 g)

(ii) 2.5 litres of 5M NaOH (**Ans.** 500 g)

(iii) 500 mL of 0.2M H_2SO_4 (**Ans.** 9.8 g)

3.22 A solution is 0·500 M in HCl. How would you prepare 1000 mL of a 0.200 M solution of HCl by diluting the original solution ?
(**Ans.** Dilute 400 mL 0.500 M HCl to 1000 mL)

3.23 An aqueous solution of sodium chloride contains 8.00 g of it per 100 g of solution at 298K. Calculate the molality of this solution.
(**Ans.** 1.487 *m*)

3.24 A solution was made by dissolving 100 g of $MgSO_4$ in 90·0 g of water and has a density of 1.10 g/cm³. Calculate the molality and molarity of the solution. (**Ans.** m=0.923, M=0·94)

3.25 Calculate the osmotic pressure of a solution containing 3 g of glucose (mol mass=180) in 60 g of water at 15°C. (**Ans.** 6.57 mm)

3.26 4 g of substance dissolved in 100 mL of water gave rise to an osmotic pressure of 5.1 atm at 22°C. Calculate the molecular mass of the substance. (**Ans.** 189.7)

3.27 The vapour pressure of water at 20°C is 17 mm. Calculate the vapour pressure of a solution containing 2 g of urea in 50 g of water.
(**Ans.** 16.8 mm)

3.28 A solution of 0.450 g of urea in 22·5 g of water gave a boiling point elevation of 0.170K. Calculate the experimental molal elevation constant of water (Molecular mass of urea=60). (**Ans.** 0.51 K/*m*)

3.29 When 0·25 g of a substance was dissolved in 100 g of water, the freezing point of the latter was lowered by 0.43K. Find the molecular mass of the substance $\left(K_f \text{ for water}=1.85\frac{K}{m}\right)$. (**Ans.** 107.5)

3.30 A solution contains 7 g of a non-volatile solute in 250 g of water and it boils at 373.52 K. Calculate molecular mass of the solute (K_f for water =0·52 K/*m*).
(**Ans.** 56)

3.31 A solution of 0.25 g of a substance in 25 g of benzene lowers the freezing point by 0.40K. Calculate the molecular mass of the substance (K_f for benzene=5.12 K/*m*)
(**Ans.** 128)

3.32 What is the molarity of a 20·0% H_2SO_4 solution if its density is 1.14 g cm^{-3}? (Ans 2.32M)

3.33 Calculate the normality and molarity of a solution containing 30 g oxalic acid ($H_2C_2O_4 . 2H_2O$) per litre. (Ans. 0·476 N 0·238 M)

3.34 Calculate the osmotic pressure of a solution containing 34.2 g of cane sugar (molecular mass 342) in 1000 g of water at 300 K. (Ans. 2.46 atm)

3.35 An aqueous solution contains 5 g of an organic substance per litre of the solution. Its osmotic pressure is found to be 0.59 atm at 280 K. Calculate the molecular mass of the substance. (Ans. 194.6)

ANSWERS TO SELF ASSESSMENT QUESTIONS

3.1 (*i*) b (*ii*) c (*iii*) a (*iv*) b
(*v*) d (*vi*) c (*vii*) a (*viii*) a
(*ix*) c (*x*) d

3.2 (*i*) saturated solution (*ii*) Raoult's law
(*iii*) mole fraction (*iv*) concentration, colligative
(*v*) positive, higher (*vi*) moles, per litre
(*vii*) moles, per kilogram (*viii*) partial pressure
(*ix*) lowered, solute (*x*) molarity, absolute temperature

3.3 (*i*) T (*ii*) T (*iii*) F (*iv*) T
(*v*) F (*vi*) F (*vii*) T (*viii*) F
(*ix*) T (*x*) T

3.4 (*i*) A pure liquid and its solid have the same vapour pressure at the freezing point. Pure water and ice have the same vapour pressure at 0°C, but the water in a solution has a lower vapour pressure than ice at this temperature. Consequently if ice and an aqueous solution at 0°C are placed in contact, the ice melts.

(*ii*) We know like dissolves like. Water being polar in nature dissolves many of the polar compounds. Stirring brings unsaturated solution in contact with the solute and thus increases the rate of solution. Further with the increasing number of ions in solution collisions between dissolved ions and solid occur. This also helps in increasing the solubility.

(*iii*) The boiling point of the liquid mixture is the temperature at which the total vapour pressure of the mixture is equal to the atmospheric pressure.

(*iv*) Energy is absorbed in overcoming the forces which hold the molecules, atoms or ions in their lattice positions in the crystal. This is, because of the absorption of energy an endothermic change that accompanies the dissolution of all solids in liquids.

(*v*) Solubilities of gases in all solvent increase as the partial pressures of the gases increase.

(*vi*) When a solute is dissolved in a liquid, some of the total volume of the solution is occupied by solute molecules and there are therefore fewer solvent molecules per unit area at the surface. As a result, solvent molecules vaporize at a slower rate than if no solute were present. This results in lowering the vapour pressure.

(*vii*) The vapour pressure of a solvent at a given temperature is lowered by the presence of a non-volatile solute in it, and such a solution must be heated to a higher temperature than a pure solvent in order for its vapour pressure to equal atmospheric pressure. At the

freezing point, the forces of attraction among molecules are just enough to cause a phase change from the liquid to the solid state. The solvent molecules in a solution are somewhat more separated because of the presence of non-volatile solute particles than they are in the pure solvent. As a result, the temperature of the solution must be lowered below the freezing point of the pure solvent in order to freeze it.

(*viii*) Colligative properties depend upon the number of solute particles in a given amount of solute. In the presence of an electrolyte say KBr, the magnitude of freezing point depression will be more as compared to a non-electrolyte because KBr will provide two particles.

(*ix*) Because of ion association, ions behave as a single particle and this tends to reduce the effective molality and therefore the freezing point depression.

(*x*) Osmosis is the spontaneous process by which solvent molecules migrate through a semipermeable membrane from a solution of lower concentration into a solution of higher concentration.

Osmotic pressure is a measure of the forces that unite solvent molecules together, thereby causing molecules of the pure solvent to migrate through the membrane into the solution in order to replace those that have been tied up by interactions with the solute.

□ □

UNIT 4
Chemical Thermodynamics

Die Energie der Welt ist constant
Die Entropie der Welt strebt einem Maximum Zu.

—R.J. CLAUSIUS (1865)

UNIT PREVIEW

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Understand various terms used in thermodynamics.
2. Calculate the change in internal energy when a system exchanges heat with the surroundings or work is done by the system on the system.
3. State and understand the first law of thermodynamics.
4. Solve problems based on the first law of thermodynamics.
5. Distinguish between heat of a reaction at the constant volume or constant pressure.
6. Calculate ΔH and ΔE.
7. Calculate standard heats of reactions, ΔH° for the processes if given appropriate standard heats of formation, ΔH_f° and description of the chemical processes.

8. Calculate bond energies from thermodynamic data.
9. Define entropy and predict spontaneity of chemical and physical changes.
10. State and explain the second law of thermodynamics.
11. Demonstrate your familiarity with free energy and its relation with maximum work.
12. Calculate $\Delta G°$ for a reaction from tabulated values of $\Delta G°$.
13. Give the relationship between free energy change and equilibrium constant.
14. State and explain the third law of thermodynamics.

4.1. INTRODUCTION

While studying chemistry it is natural to ask why certain chemical reactions take place and others do not. There are two factors that determine whether or not a particular reaction would take place of its own without the help of an external source. You may recall that most of the physical and chemical changes are accompanied by energy changes. **Thermodynamics is the study of energy exchanges.** Laws of thermodynamics discussed in this unit answer the question, "**Will the reaction take place by itself, without outside help ?**".

Chemical thermodynamics provides informations about (*i*) energy evolved or absorbed during a reaction, (*ii*) increase/decrease of the disorder, (*iii*) spontaneity of a reaction, and (*iv*) the extent to which a reaction takes place.

4.2. SOME COMMONLY USED TERMS

In the study of chemical thermodynamics the following terms are frequently used.

System. It is any part of the universe which is selected within a definite boundary for investigations.

Surroundings. The whole of the universe which is around the system is known as surroundings. A system may exchange matter and energy with the surroundings. For example, consider a reaction taking place in a conical flask, here the conical flask and everything else around the reaction mixture are considered the surroundings.

A system, in general, can be of three types :

(*i*) **Open System.** A system which can exchange both matter as well as energy with its surroundings is called an open system. Consider evaporation of water kept in a beaker (Fig. 4.1). Here water takes heat from the surroundings and evaporates. Water vapour can also condense into it. Thus, it is an open system.

(*ii*) **Closed System :** A system which can exchange energy but not matter with its surroundings is called a closed system. For example, heating water in a closed vessel (Fig. 4.2). Here, heat

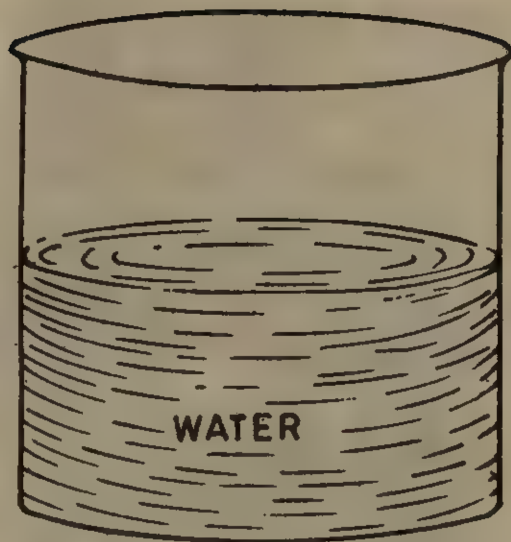


Fig. 4.1. An open system.

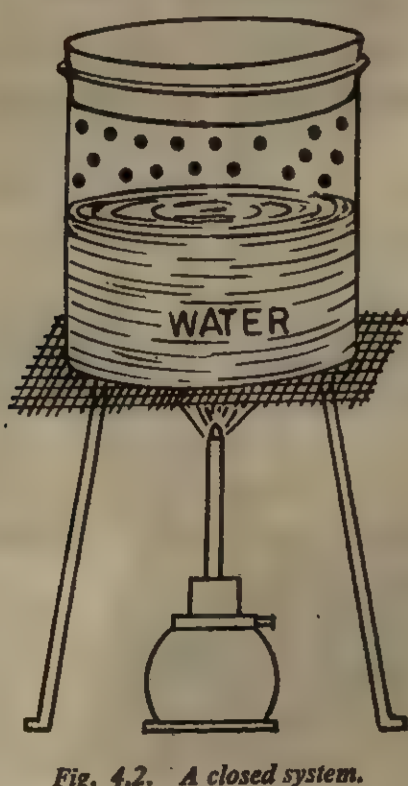


Fig. 4.2. A closed system.

energy can enter and escape from the system but not water vapours. Matter can neither be added to nor removed from it.

(*iii*) **Isolated System :** A system which can exchange neither energy nor matter with its surroundings is called an isolated system. For example, water kept in a perfectly insulated thermos flask. As flask is insulated and stoppered, exchange of energy and matter with the surroundings is not possible.

Adiabatic Change. If a change takes place in such a way that there is no exchange of heat between the system and its surroundings, the change is said to be adiabatic. Adiabatic conditions can be achieved by insulating the interface or boundary between the system and its surroundings. For example, a reaction carried out in a thermoflask.

Isothermal Change. The chemical or physical changes, where the system and the surroundings are in thermal contact and heat is exchanged between the two in such a way that the temperature remains constant, are known as isothermal changes.

Any process that releases heat from the system to the surroundings is referred to as **exothermic** [Fig. 4.3(*a*)]. And a process in which the system absorbs heat from the surroundings is called **endothermic** [Fig. 4.3(*b*)].

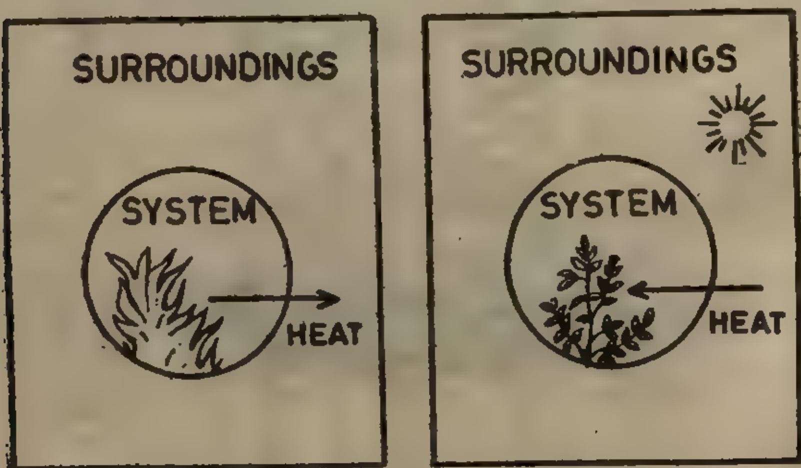


Fig. 4.3(a) Exothermic process. *Fig. 4.3(b) Endothermic process.*

State Variables or Functions. A system is normally characterized in terms of its mass, volume, density, temperature, pressure, *etc.* These properties can be easily measured and called as state variables or state functions. The values of state variables depend upon the state of the system, and not on the process through which the state is achieved. For example, one has to go to the eighth floor of a building located at a height '*l*' metres from the ground

floor. Height, *l* m is a state variable because its value depends on the location of the eighth floor. It is independent of whether you go by stairs or by a lift. However, the time taken to reach the eighth floor is not a state variable as it will depend whether you are going by lift or by stairs.

State variables are important and useful because changes in their values depend only on the initial and the final states of a system and not on how the changes are carried out. When these variables are specified, the state of the system is known precisely.

Extensive and Intensive State Variables : When the magnitude of a state variable is independent of the size of the system, it is known as **intensive state variable** *e.g.*, temperature, pressure, concentration, density, refractive index, *etc.*

The value of an **extensive variable** depends on the size of the system and as the size grows the value of this variable also increases, *e.g.*, volume, mass, surface area, absorption of a gas by charcoal *etc.*

Exercise 4.1. *Classify the following into extensive or intensive variables* : (*i*) *density*, (*ii*) *energy*, (*iii*) *enthalpy*, (*iv*) *boiling/melting point*, (*v*) *molar mass*, (*vi*) *dipole moment*, (*vii*) *surface tension*, (*viii*) *vissocity*, (*ix*) *refractive index*, *and* (*x*) *heat capacity*.

Solution. Extensive variables : (*ii*), (*iii*) and (*x*). Rest all are intensive variables.

Reversible and Irreversible Processes. A reversible process is one in which the change is carried out so slowly that the system and the surroundings are always in equilibrium. In an irreversible process, the change is brought about very quickly and there is no equilibrium between the system and the surroundings. A gas can be expanded and compressed reversibly under isothermal conditions while adiabatic expansion and compression of a gas will be irreversible process.

4.3. INTERNAL ENERGY, *E*.

The internal energy, *E*, of a thermodynamic system is the sum of all the types of energies its constituents can possess. This includes all possible forms of energies of the system. The internal energy of a system is made up of a number of components such as :

(*i*) the translation energy of molecules,

(*ii*) the rotational energy of molecules,

(*iii*) the vibrational energy of molecules,

(*iv*) the coulombic energy between the electrons and the nuclei in atoms, and

(*v*) the interaction energy of the constituent molecules of the system (Fig. 4·4).

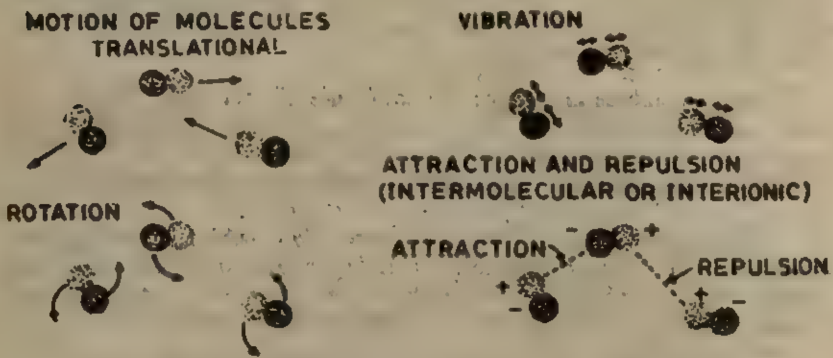


Fig. 4.4. Contributions to internal energy.

The absolute value of internal energy cannot be determined. However, the change in internal energy, ΔE, can be experimentally measured from the change in the properties of the system.

$$\Delta E = \Sigma E_{(products)} - \Sigma E_{(reactants)} \quad ...(4.1)$$

The internal energy of a system depends upon the state of the system and not upon how the system attains that state. Internal energy is, therefore, a state function.

An increase in the internal energy of a system may possibly result in :

(*i*) an increase in the temperature of the system,

(*ii*) the change in its physical state—melting, vaporization or change in crystalline form or

(*iii*) a chemical reaction.

Experiment 4.1.

Take a sample of an ideal gas that occupies a volume of 1 litre at 300K and 1 atm pressure; let it be its state I. At 600K and 0.5 atm, the gas occupies a volume of 4 litres (its state II). Let us denote internal energies in state I and II by E_I and E_{II}, respectively. The difference of internal energy in these two states is,

$$\Delta E = E_{II} - E_I \quad ...(4.2)$$

State II can be achieved by different paths starting from state I. First path may include the heating of the gas to 600 K and then reducing the pressure to 0 5 atm. Second path may be envisaged as first decreasing the pressure to 0.5 atm and then raising the temperature to 600K. Both the paths can be performed in terms of a number of intermediate steps. The change in internal energy in either case is the same because the initial and the final states of the system are the same.

4.4. THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is also called the law of conservation of energy, it states, "**Energy in an isolated system can neither be created nor destroyed**". Energy can be converted from one form to another, but cannot be destroyed. **The energy of universe is constant.**

The internal energy of a system can be changed in two ways, (*i*) either by allowing heat to flow into the system or out of the system, and (*ii*) by work done on the system or by the system. Let us consider a system whose internal energy be E_1. If the system is supplied a certain amount of heat, q, the internal energy of the system will increase to E_1+q. If work (w) is now done on the system, the internal energy in the final state of the system, E_2 will be given by

$$E_2=E_1+q+w \qquad ...(4.3)$$

or

$$E_2-E_1=q+w$$

$$\Delta E=\overset{heat}{q}+\underset{work}{w} \qquad ...(4.4)$$

This is the mathematical form of the first law of thermodynamics which gives the relationship between internal energy, heat and work. The first law of thermodynamics is usually stated as, "**The change in internal energy of a system equals the heat exchanged by the system plus the work done on or by the system.**"

4.4.1. Sign Conventions

In equation (4.4) ΔE is positive when system gains energy. To do this, **heat** that has been **added to the system** and **work** that has been **done ont he system**—both of these, which increase the internal energy of the system are given **positive values. Heat lost** by a system or **work done on the surroundings** by the system both decrease the internal energy of the system, and are given **negative signs.**

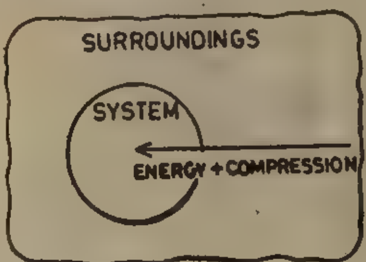


Fig. 4.5(a). Energy of system increases ΔE is positive; $(q+w) > 0$

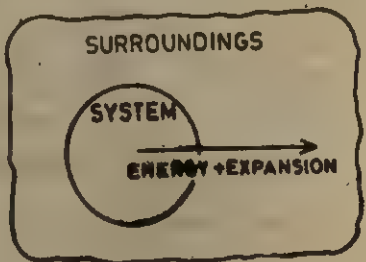


Fig. 4.5(b). Energy of system decreases ΔE is negative ; $(q+w) < 0$

It should be noted that q and w are not state functions. This is because the values of q and w depend upon the way in which the change is carried out. The essence of equation (4.4) is that though q and w are not state functions, $q+w(=\Delta E)$ is a state function, *i.e.*, $(q+w)$ does not depend upon how a change is brought about.

If a system undergoes a change in such a way that its internal energy remains the same ($\Delta E=0$). Then,

$$q=-w \qquad \ldots(4.5)$$

For such a change, the heat absorbed by the system is equal to the work done by the system.

Work. Two main types of work are normally involved in chemistry. These are (*i*) electrical work, and (*ii*) mechanical work. Electrical work is important in systems where reactions occur between ions while a mechanical work is involved when a system changes its volume against an externally applied pressure.

Mechanical work is specially important in systems that contain gases. In the reactions involving gases, volume changes occur at constant pressure. In a closed vessel fitted with a piston, the supply of heat will change its volume and some work will be done by the system. This work is referred to as pressure-volume work.

4.4.2. Pressure-Volume Work

Consider a system consisting of a cylinder 'C' of cross-section area A fitted with a frictionless and weightless piston F. When the piston has position as shown by yy^1 (Fig. 4.6) pressure inside the

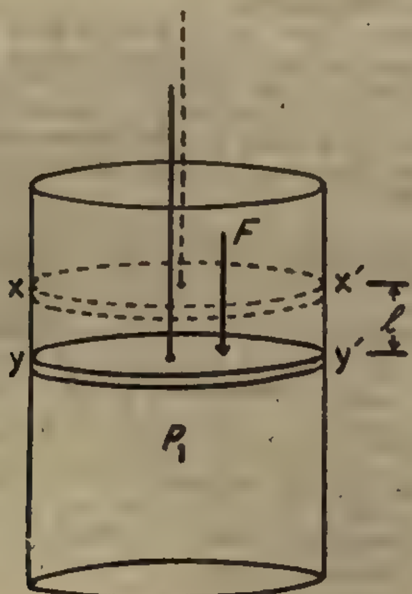


Fig. 4.6. Pressure-volume work.

cylinder and atmospheric pressure are P_1 and P respectively. Let P_1 be greater than P then the piston will move upward till the pressure inside the cylinder is also P atm. The new position of the piston is xx' and it has moved to a distance l. In this process, the gas inside the cylinder did work against the atmospheric pressure, P.

The work done by the gas, ⇒, the work done by the piston on the surroundings in moving from the initial position yy' to the final position xx'. Let this work be w. You know

$$\text{Work} = \text{Force} \times \text{distance}$$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

or Force=Pressure × Area. Substituting the values

$$w = P \times A \times l = P \times A \, . \, l$$

Here $A \, . \, l$=change in volume of the gas, ΔV.

Thus

$$w = P \times \Delta V$$

If the piston moves reversibly, *i.e.* very very slowly against the constant pressure P then the work done by the piston on the surroundings, dw is given by

$$dw = PdV \qquad \text{...(4.6)}$$

where dV is a very very small change in volume.

Thus total work done $w_{rev.}$ can be calculated by integrating the equation (4·6) when volume changes from V_1 to V_2, we have

$$w_{rev.} = \int_{V_1}^{V_2} P \, dV$$

or
$$w_{rev.} = \int_{V_1}^{V_2} nRT \frac{dV}{V} \qquad \left(\because \; P = \frac{nRT}{V} \right)$$

or
$$w_{rev.} = 2{\cdot}303 \, nRT \log \frac{V_2}{V_1} \qquad \text{...(4.7)}$$

Exercise 4.2. *For each of the following chemical and physical changes at constant pressure, is work done by the system (the substances undergoing the change) on the surroundings or by the surroundings on the system ?*

(*i*) $C(s) + O_2(g) \rightarrow CO_2(g)$

(*ii*) $N_2O_4(g) \rightarrow 2NO_2(g)$

(*iii*) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(*iv*) $H_2O(l) \rightarrow H_2O(g)$

Solution.

(*i*) There is one mole of gaseous reactant which changes to 1 mole gaseous product *i.e.* $\Delta V=0$, this the amount of work done is negligible.

(*ii*) One mole of gaseous reactant forms 2 moles of gaseous products. There is increase in the volume, thus system does work on the surroundings, w is negative.

(*iii*) 4 moles gaseous reactants change to 2 moles gaseous products, volume decreases. In this case surroundings does work on the system, w is positive.

(*iv*) Volume increases, system does work on the surroundings, w is negative.

Exercise 4.3. *In a single process, a system does 120 J of work on the surroundings while 55 J of heat is added to the system. What is the internal energy change for the system ?*

Solution. A system loses energy when it does work on the surroundings, therefore $w=-120$ J. When heat is added to the system, it increases its internal energy, therefore, $q=+55$J We know

$$\Delta E=q+w$$

Substituting the values,

$$\Delta E=55-120=-65 \text{ J}$$

The internal energy of the system decreases by -65 J.

Exercise 4.4. *One mole of nitrogen at 300K expands isothermally from 3* atm. *to 1* atm. *Assuming that nitrogen gas behaves ideally, calculate w, if the expansion is* (*i*) *single step, and* (*ii*) *reversible against a constant pressure of 1* atm.

Solution. The initial volume of the gas$=V_1$ is given by

$$V_1=\frac{nRT}{P}=\frac{1\times 0{\cdot}082 \text{ dm}^3 \text{ atm } K^{-1} \text{ mol}^{-1}\times 300\ K}{3 \text{ atm.}}$$

$$=8.21 \text{ dm}^3$$

Similarly the find volume V_2 at 1 atm. will be 24.63 dm^3

(*i*) $$w=P\Delta V=P\,(V_2-V_1)$$
$$=(101.325 \text{ N}m^{-2})\ (16.42\times 10^{-3}\text{m}^3)$$
$$=101.325\times 16.42 \text{ N } m=1{\cdot}663 \text{ kJ}$$

(*ii*) $$w_{rev}=2.303\ nRT\log\frac{V_2}{V_1}$$

$$=2.303\times 1\times 8.31 \text{ J}k^{-1}\text{ mol}^{-1}\times 300\text{K }\log\frac{24.63}{8.21}$$

$$=2.74 \text{ kJ}$$

When a closed system absorbs heat, q, some of the energy is consumed in increasing the internal energy, ΔE of the system and

the rest is used up in doing pressure-volume work $P\Delta V$.

Therefore, $q = \Delta E + P\Delta V$ ...(4.8)

If the volume remains constant,

i.e., $\Delta V = 0$,

or $q_v = \Delta E$ ...(4.9)

The total heat supplied to the system at a constant volume is used up in increasing the internal energy of the system.

Exercise 4.5. *Calculate the amount of heat produced from the combustion of 1.6 g of methane which burns in oxygen according to the following equation :*

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + 2100 \text{ KJ}$$

Is this reaction endothermic or exothermic ?

Solution. 16g CH_4 on combustion gives 2100 kJ heat. Therefore, 1.6g CH_4 on combustion would produce heat $= (2100/16) \times 1.6 = 210$ kJ. Since heat is given off, $q = -210$ kJ, has negative sign.

Reaction is exothermic *i.e.* heat is given out.

Several reactions are carried out under constant volume conditions, *e.g.*, determination of calorific value of a fuel in bomb calorimeter. In such cases the system does some useful work referred to as work of non-expansion.

A chemical change performed in a bomb calorimeter takes place under constant volume conditions. Bomb calorimeter is

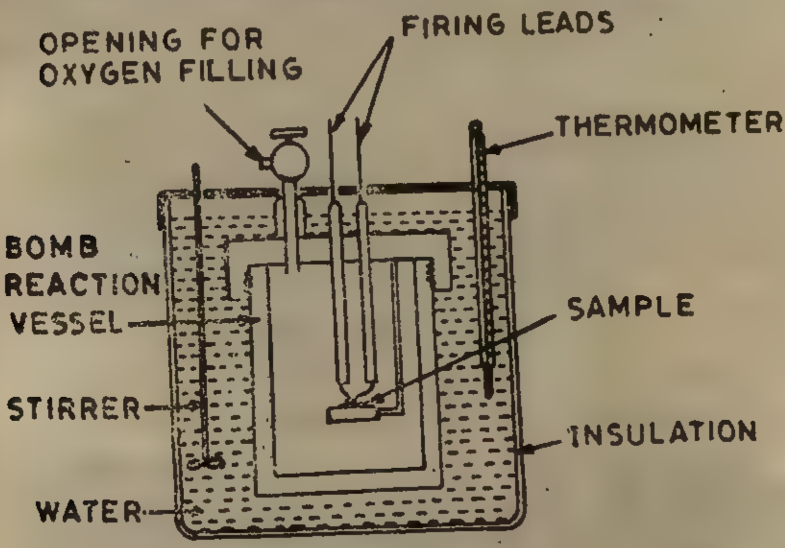


Fig. 4.7 Bomb calorimeter

generally used to find out the calorific values of a fuel or any combustible substance. Figure 4.7 describes the main parts of a bomb calorimeter.

4.5. ENTHALPY AND ENTHALPY CHANGES

4.5.1. Meaning of Enthalpy, *H* :

When a reaction is carried out at constant volume, the energy change is designated by ΔE. However, we generally carry out reactions at constant pressure *i.e.*, at atmospheric pressure. Consider the energy change associated with the reaction between calcium carbonate and dilute hydrochloric acid at the room temperature

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

If the reaction is carried out at constant pressure, *e.g.*, in the apparatus shown in Fig. 4.8, then the gas carbon dioxide evolved does work against the atmospheric pressure by pushing the piston outward. In the form of work, equivalent amount of energy is transferred to the surroundings.

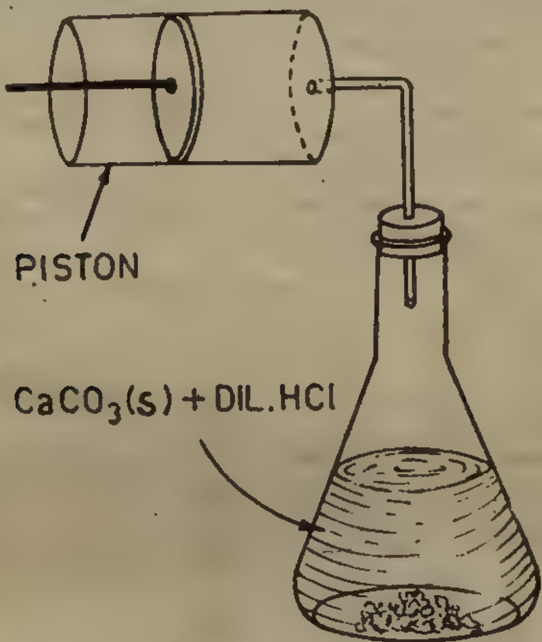


Fig. 4.8. Reaction at constant pressure.

Thus, ΔE which we measure will not be a true representation of the internal energy change, because some energy is being used up in doing this mechanical work. We have to take into account also the energy associated with this mechanical work. If the reaction proceeds with decrease in volume, the work is done by the surroundings

and in the process the energy equivalent of this pressure-volume work is transferred to the system. To handle such situations another property known as enthalpy, ,H is associated with every substance. **The enthalpy, H, of a substance is defined as the sum of the internal energy and pressure-volume, PV, energy associated with it,** *i.e.*,

$$H = E + PV \qquad \ldots(4.10)$$

Let us consider that when under conditions of constant pressure, P, and temperature, T, a system absorbs q_p joules of heat, its volume increases by ΔV and internal energy increases by ΔE. We further assume that work other than pressure-volume work performed is zero, then from equation (4.11), we have

$$\Delta H = \Delta E + P\Delta V \qquad \ldots(4.11)$$

If heat absorbed at constant pressure and constant temperature is q_p then

$$q_p = \Delta E + P\Delta V \qquad \ldots(4.12)$$

or

$$q_p = \Delta H \qquad \ldots(4.13)$$

i.e., **heat absorbed, q_p, under conditions of constant pressure, and temperature is a measure of change in enthalpy, ΔH, of the system.**

4.5.2. Enthalpy Change, ΔH

A substance has a definite amount of energy stored in it which is called its enthalpy or heat content* symbolized by H. It is not possible to measure enthalpy of a substance, but the enthalpy change, ΔH, which it undergoes in a physical or chemical change can be measured. The energy change at a constant pressure and temperature is called the enthalpy change, ΔH; it is equal to the amount of heat exchanged with the surroundings at a constant pressure and constant temperature. While studying the enthalpy change for a reaction, the apparatus is well insulated and temperature is allowed to change. Then the products are brought back to the temperature of the experiment and the heat exchange involved in this process is also taken into account. Though the absolute value of enthalpy, H, cannot be measured, yet it is possible to measure the enthalpy change associated with a chemical reaction. Tihs represents the difference between the enthalpies of the products and the reactants.

$$\Delta H = \Sigma H_{(\text{products})} - \Sigma H_{(\text{reactants})} \qquad \ldots(4.14)$$

Equation (4.13) is important because it shows that when we measure a heat change at constant pressure we are actually measuring a change in the enthalpy. The change in enthalpy is determined calorimeterically.

* Heat content of an element or compound depends upon pressure and temperature. To compare change in heat, ΔH, the temperature and pressure must be identical. For this purpose a standard state is defined, when enthalpy change is measured at 298 K and 1 atm pressure, the substances are said to be in the standard state.

4.5.3. Relationship between ΔH and ΔE

The difference between ΔH and ΔE is not usually significant for solids or liquids but it is significant for gases.

Consider a reaction which involves gases. If V_r is the total volume of the reactants, V_P is the total volume of the products, n_r is the number of moles of the reactants, n_p is the number of moles of the products, all at constant pressure P and temperature T. Then ideal gas law gives,

$$PV_r = n_r RT$$

and $$PV_p = n_p TR$$

Thus, $PV_p - PV_r = n_p RT - n_r RT = (n_p - n_r)\,TR$

or $$P\Delta V = \Delta n RT \qquad ...(4.15)$$

Substituting the value of $P\Delta V$ in equation (4.11)

$$\Delta H = \Delta E + \Delta n RT \qquad ...(4.16)$$

The above equation is useful for converting ΔH into ΔE or vice versa.

Exercise 4·6. *In the reaction,* $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$; 335 kJ *heat is evolved. What is the value of* ΔH ?

Solution. Since the reaction tak·· place with the evolution of heat, heat content of products would be less than that of the reactants. Thus,

$$\Delta H = -335 \text{ kJ}.$$

Exercise 4·7. *When 1 mole of methane is burnt in oxygen under standard conditions (101.325 Nm⁻² and 298k)*, in a bomb calorimeter the heat evolved is *885·0* kJ, *i e.*

$$\Delta E = -885{\cdot}0 \text{ kJ}.$$

How much heat would be evolved if the same reaction were carried out at constant pressure ?

Solution. The equation for reaction is

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The volume of the liquid can be considered as negligible, then

Δn = number of moles of products − number of mole· ·eactants

$$= 1 - (1+2) = -2$$

We know

$$\Delta H = \Delta E + \Delta n RT.$$

Substituting the values

$$\Delta H = -885 \text{ kJ} + [(-2 \text{ mol}) \times 8{\cdot}31 \times 10^{-3} \text{ kJ m}\quad{}^{1}\text{K}^{-1} \times 298\text{K}]$$

$$= -885 \text{ kJ} - 4{\cdot}96 \text{ kJ} = -889.96 \text{ kJ}$$

4 6. APPLICATION OF FIRST LAW OF THERMODYNAMICS

(*i*) **Internal Energy Change.** The first law of thermodynamics enables us to calculate internal energy change in a reaction-physical or chemical, when there is,

(*a*) exchange of energy with the surroundings,

(*b*) volume change in the reaction.

The use of the first law of thermodynamics in the calculation of internal energy is illustrated in the following exercise.

Exercise 4.8 *A gas absorbs 1·20* kJ *of heat and is compressed from 20.0* dm^3 *to 10·0* dm^3 *by an opposing pressure of 100*kPa. *What is* ΔE *for this process ?*

Solution: We know

$$\Delta E = q + w$$

$q = +1.20$ kJ (heat absorbed by the system is positive)

$$w = P_{opp}\,(V_{final} - V_{initial})$$

$$= 100\ kPa\ (20.0\ dm^3 - 10.0\ dm^3)$$

$$= (100 \times 10^3\ Nm^{-2})(10.0 \times 10^{-3} m^3)$$

$$= 1000\ Nm = 1.0\ kJ$$

(w is positive because the work is done on the system)

Substituting the values of q and w, we have

$$\Delta E = 1.20\ kJ + 1.0\ kJ = 2.20\ kJ.$$

(*ii*) **Enthalpies Change in Reactions,** ΔH. Enthalpy change for a reaction which takes place in several steps can be calculated using Hess' law of constant heat summation which is a direct consequence of the first law of thermodynamics.

The use of Hess' law in the calculation of enthalpies of reactions is illustrated below :

Exercise 4.9. *Given the enthalpy changes for the following two reactions :*

(*i*) $N_2(g) + O_2(g) \rightarrow 2NO(g)$; $\Delta H = 180.50$ kJ

(*ii*) $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$; $\Delta H = 114.1$ kJ.

Find the heat of reaction for

$$N_2(g) + 2O_2(g) = 2NO_2(g)\ ;\ \Delta H = ?$$

Solution. Attempt should be made to get the desired equation from the given reactions. On examining the reactions (*i*) and (*ii*), you can see that in the reaction (*ii*) $2NO_2(g)$ is on the LHS whereas in the desired reaction $2NO_2(g)$ is on the RHS. Therefore, write reaction (*i*) as it is but reaction (*ii*) in the reverse manner, we have.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)\ ;\ \Delta H = 180{\cdot}0\ kJ$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)\ ;\ \Delta H = -114.1$$

Now on adding these two reactions, we have

$$N_2(g) + O_2(g) + 2NO(g) + O_2(g) = 2NO(g) + 2NO_2(g)$$

or $$N_2(g) + 2O_2(g) = 2NO_2(g)$$

Therefore

$$\Delta H = 180.0\ kJ - 114.1\ kJ = 65.9\ kJ$$

4.6.1. Calculation of Enthalpy Change ΔH for a Reaction from the Standard Heat of Formation, ΔH°_f.

Standard heat of formation of a chemical compound is the heat of reaction in which one mole of the compound is formed from its constituent elements in their most stable forms at 298.2K and 1 atmospheric pressure. The enthalpy of pure elements in their stable and standard state is always taken as zero. For example, the enthalpy of carbon is zero for graphite at 298·2K and 1 atmospheric pressure. The standard enthalpies of formation of some of the compounds are given in Table 4.1.

The enthalpy change of any reaction is given as :

$$\Delta H_{reaction} = (\text{sum of } \Delta H^\circ_f \text{ of products}) - (\text{sum of } \Delta H^\circ_f \text{ of reactants}) \quad ...(4.14)$$

Table 4.1 Standard enthalpies of formation at 298.2 K

Substance	ΔH° (kJ mol^{-1})	*Substance*	ΔH° (kJ mol^{-1})
$H_2(g)$	0.0	$Br_2(g)$	30.71
$H(g)$	217.7	$I_2(s)$	0.0
$H_2O(l)$	−286.0	$I_2(g)$	62.26
$H_2O(g)$	−241.8	$Cl(g)$	121.4
$H_2O_2(l)$	−188.0	$Br(g)$	111.8
$C(g)$	718.4	$I(g)$	106.6
C (diamond)	1.896	$HF(g)$	−268.6
C (graphite)	0.0	$HCl(g)$	−92.30
$CO(g)$	−110.5	$HBr(g)$	−36.23
$CO_2(g)$	−393.5	$HI(g)$	25.44
$CH_4(g)$	−74.85	$H_2S(g)$	−20.17
$C_2H_6(g)$	−84.68	S(rhombic)	0.0
$C_2H_4(g)$	52.30	S(monoclinic)	0.2971
$C_2H_2(g)$	226.7	$SO_2(g)$	−296.9
$C_6H_6(l)$	49.04	$CaCO_3$(calcite)	−1207
$C_6H_6(g)$	82.93	$Hg(l)$	0.0
$N(g)$	472.7	$Hg_2Cl(s)$	−264.9
$NO(g)$	90.37	$NaCl(s)$	−411.0
$NO_2(g)$	33.85	$Na_2CO_3(s)$	−1131
$N_2O(g)$	81.85	$KCl(s)$	−435.9
$NH_3(g)$	−46.19	$KNO_3(s)$	−492.7
$O_3(g)$	142.3	$AgCl(s)$	−127.0
$O(g)$	247.5		
$OF_2(g)$	23.0		

(Heat of formation of an element in its standard state is zero.)

Exercise 4.10. *Using standard enthalpy of formation from Table 4.1 calculate the enthalpy change for the reaction*

$$2H_2S(g)+3O_2(g) \rightarrow 2H_2O\ (l)+2SO_2(g)$$

Solution. Equation (4.14) implies that

$$\Delta H_{\text{reaction}} = (\text{sum of } \Delta H^\circ_f \text{ products}) - (\text{sum of } \Delta H^\circ_f \text{ reactants})$$

Therefore, $\Delta H_{\text{reaction}} = [\Delta H^\circ_f H_2O\ (l) + 2\Delta H^\circ_f SO_2(g)] - [2\Delta H^\circ_f H_2S(g) + 3\Delta H^\circ_f O_2(g)$

Substituting ΔH°_f values from Table 4.1 we have

$$\Delta H_{\text{reaction}} = [2\times(-286\ 0)+2\times(296\text{·}9)]-[2\times(-20.17)+3\times 0]$$
$$=[-572-593.8]+40.34\ \text{kJ} = -1125.46\ \text{kJ}$$

(Remember that ΔH°_f for an element is always zero)

4.6.2. Calculation of Bond Energy : The bond energy of a diatomic molecule is defined as the enthalpy change when one mole of gaseous molecules are dissociated into atoms. For emample, bond energy of H_2 and Cl_2 may be expressed as :

$$H_2(g) \rightarrow 2H(g)\ ;\ \Delta H = 435\text{·}4\text{kJ mol}^{-1}$$
$$Cl_2(g) \rightarrow 2Cl(g)\ ;\ \Delta H = 243\text{kJ mol}^{-1}$$

The positive sign of ΔH indicates that process of bond dissociation is endothermic. The bond energy of diatomic molecules containing two different atoms can be calculated using Hess' law. For example, bond dissociation energy of HCl molecules is,

$$HCl \rightarrow H(g)+Cl(g),\ \Delta H = 243\ \text{kJ mol}^{-1}$$

We know from Table 4.1, the enthalpy of formation of

$$HCl(g) = -92.3\ \text{kJ mol}^{-1}$$
$$H\ (g) = 217.7\ \text{kJ mol}^{-1}$$
$$Cl(g) = 121.4\ \text{kJ mol}^{-1}$$

We can now write

$$\Delta H = \Sigma\Delta H^\circ_f \text{ products} - \Sigma\Delta H^\circ_f \text{ reactants}$$
$$=217.7+121.5-(-92.3)$$
$$=431.5\ \text{kJ mol}^{-1} \text{ at } 298.2\ \text{K}$$

For a molecule containing several bonds of one type, the bond dissociation energy is not the same for the successive bonds. For example, in methane

$$H_3C-H = 425\ \text{kJ mol}^{-1} : H_2-C = 470\ \text{kJ mol}^{-1}$$
$$HC-H = 416\ \text{kJ mol}^{-1}\ ;\quad C-H = 335\ \text{kJ mol}^{-1}$$

However, in such cases an average bond energy is assigned to an individual bond by taking average of the dissociation energies of the bonds involved. For example C—H bond energy

$$= \frac{425+470+416+335}{4} = 411\text{·}5\ \text{kJ mol}^{-1}$$

The values of some common bond energies are given in the Table 4.2.

Table 4.2. Bond energies

Bond	*Bond energy** (kJ mol^{-1})	*Bond*	*Average bond energy*** (kJ mol^{-1})	*Bond*	*Average bond energy*** (kJ mol^{-1})
H–H	436	O–O	138	C–H	485
H–F	565	N–N	159	C–Cl	326
H–Cl	431	N=N	418	C–O	335
H–Br	364	C–C	347	C=O	707
H–I	297	C=C	619	C–N	293
F–F	155	C≡C	812	C=N	616
Cl–Cl	242	O–H	463	C≡N	879
Br–Br	190	N–H	389		
I–I	149	C–H	413		
O=O	494				
N≡N	941				

* These bond energies are the dissociation energies of diatomic molecules that have only one bond ; they are, therefore, exact values.

** These bond energies are obtained from molecules that contain more than one bond ; therefore, they are average values.

Exercise 4.11. *Calculate the ΔH for the reaction*

$$\begin{array}{c} H \\ | \\ H-C-Cl(g) \\ | \\ Cl \end{array} \rightarrow C\,(g)+2H(g)+2Cl(g)$$

The average bond energies of C–H bond and C–Cl bond are 415.0 kJ mol^{-1} *and 326.0 kJ mol^{-1} respectively.*

Solution. ΔH of the reaction can be calculated if we know the heat of formation of each species taking part in the reaction. The $\Delta H^0{}_f$ for CH_2Cl_2 can be calculated from the bond energies of C–Cl and C–H bonds. The formation of this compound involves formation of 2 C–Cl and 2 C–H bonds. As for bond formation $\Delta H^\circ{}_f$ is negative it can be written as

$$\Delta H^\circ{}_f CH_2Cl_2 = [2\times \text{bond energy of C–H bond} + 2\times \text{bond energy of C–Cl bond}]$$

Substituting the values of bond energies

$$\Delta H^\circ{}_f CH_2Cl_2 = 2\times -415 + 2\times -326$$
$$= -1482.0 \text{ kJ mol}^{-1}$$

Once we know $\Delta H^0{}_f$ for all the species involved in the reaction, ΔH for reaction can be easily calculated.

$$\Delta H_{reaction} = \Delta H^\circ{}_f C(g) + 2\Delta H^\circ{}_f H(g) + 2\Delta H^\circ{}_f Cl(g) - \Delta H^\circ{}_f CH_2Cl_2(g)$$

Substituting the values

$$\Delta H_{reaction} = (0+2\times0+0)-(-1482.0)$$
$$= 1482.0 \text{ kJ mol}^{-1}$$

Exercise 4·12. *The enthalpy change (ΔH) for the reaction $N_2(g)+3H_2(g) \rightarrow 2NH_3(g)$ is -92.38* kJ at 298 K.

What is ΔE at 298 K ?

Solution. From equation (4.13) we know,

$$\Delta H = \Delta E + \Delta nRT$$

Δn = (number of moles of products) − (number of moles of reactants)

$$= 2-4 = -2$$

Substituting the values in equation (4.13)

$$-92.38 \text{ kJ} = \Delta E + [-2\times8.31\times298\times10^{-3} \text{ kJ}]$$

or $\Delta E = -92.38 + 4.95 = -87.43$ kJ

4.7. Second Law of Thermodynamics

It is evident that the concepts of internal energy and enthalpy help us to understand the energy changes in chemical reactions. The essence of the first law is that all physical and chemical processes take place in such a manner that the total energy of the universe (*i.e.*, the sum of the energy of the system and of the surroundings) is constant. This law stands fully verified because no transformation has been observed which violates the principle of conservation of energy. **There is no such thing as a free lunch.** However, it is also observed that all processes have a natural direction, *i.e.*, a direction in which they take place spontaneously. Spontaneous processes are those which naturally occur without the aid of any external agency. Flow of heat from higher temperature to lower temperature, evaporation of water, melting of ice, dissolution of sugar in water and combination of hydrogen and chlorine in sunlight to give HCl(g) are spontaneous reactions in nature. On the other hand there are a large number of physical and chemical changes which need some external energy so that the change can take place, *e.g.*, reaction between $H_2(g)$ and $O_2(g)$, decomposition of $KClO_3$, formation of SO_3 at room temperature, *etc*. These changes are non-spontaneous.

Let us have a close look at some of the spontaneous processes. Consider the reaction between aluminium and bromine. As soon as the two come in contact, the chemical change takes place with the evolution of heat. Same thing happens when sodium or potassium is brought in contact with water. These reactions are exothermic in nature, *i.e.*, heat is evolved during the change. Now what is the relation between the enthalpy or heat content of the reactants and the products.

The energy consideration reveals that the heat content of products is less than that of the reactants. **Thus, one can safely say that the reactions in which enthalpy of products is less than that of reactants will be spontaneous.** Is it the sufficient condition for a spontaneous process? The answer is no, because, in nature, there are several reactions which are endothermic in nature yet spontaneous. In an endothermic reaction heat is absorbed, therefore, the heat content of products will be more than that of the reactants.

(*i*) Some endothermic changes proceed spontaneously. Heat is absorbed in them.

Examples

(*a*) Evaporation of water

(*b*) Dissolving of potassium nitrate in water

(*ii*) Some spontaneous chemical reactions do not go to completion.

Examples

(*a*) $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$

(*b*) $CH_3COOH(l)+C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l)+H_2O(l)$

The mixing of two gases illustrates that a change may occur spontaneously, if it leads to an increase in the disorder even if no

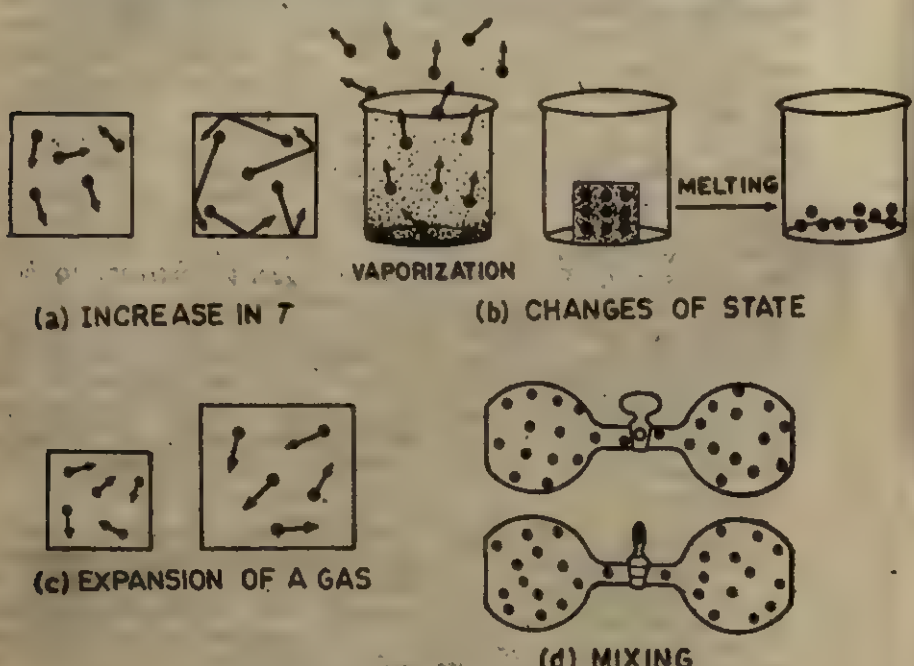


Fig. 4·9. Processes with ΔS positive

change takes place in energy of the system. It is an accepted fact that there is greater disorder in the gaseous state as compared to the liquid state. Figure 4.9 illustrates some of the processes for which $\Delta S>0$. That is why evaporation of water is a spontaneous process although it is an endothermic process.

To summarize, a transformation has a characteristic direction in which this takes place spontaneously, *i.e.*, of their own without the help of an outside agency. You know that a cup of tea can be made hot by heating, but this is not a spontaneous process because an outside agency (a gas burner) has to be used. Similarly, two gases in a mixture can be separated if allowed to diffuse through a porous plug, and a solution of sodium chloride can be made to yield hydrochloric acid and sodium hydroxide, but in each case the change has to be brought about.

There is another feature of all spontaneous changes which should be noted. A glass of hot water cools until it reaches the same temperature as the surroundings. Once the temperature becomes uniform, no further change in temperature is observed. We say that the glass of water and the surroundings are in thermal equilibrium. Mixing of two gases continues until each is evenly distributed throughout the entire apparatus. A uniform distribution is again an equilibrium situation which does not change with time. All spontaneous chemical reactions proceed until an equilibrium is achieved.

It may be concluded from the above discussion that the direction of spontaneous occurrence of a process is dictated : (*i*) by the direction in which energy is lowered, and (*ii*) by the direction in which disorder increases. An endothermic process can occur spontaneously provided the extent of disorder outweights the influence due to energy absorption. Is there any measure for disorder in a substance ?

4.7.1 Entropy and Spontaneity. The second law of thermodynamics introduces the concept of entropy in terms of which the spontaneity of a reaction can be predicted. Entropy is a measure of disorder and is a state function, *i.e.*, its value depends on the state of the system irrespective of the methods through which it is achieved. The change in entropy is mathematically represented as,

$$\Delta S=\frac{q_{rev}}{T} \quad \ldots(4.17)$$

where q_{rev} is the amount of heat supplied reversibly to the system at temperature T. (A process is said to be reversible if it is carried out so slowly that there exists an equilibrium between the system and the surroundings at every stage of the process). If $q_{rev.}$ is expressed in joule (J) and temperature in kelvin (K) the entropy change is given as JK^{-1}. One can think of entropy as a measure of the degree of randomness or disorder in a system. The greater the

disorder in a system, the higher is the entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered) ; the gaseous state is the state of highest entropy, and the liquid state is intermediate between the two.

There are many ways of stating the second law of thermodynamics. A useful form is : "**The entropy of the universe increases in the course of every spontaneous (natural) change.**" In practice, the universe means the system (*i.e.*, the content of the reaction vessel) and its surroundings.

The concept of entropy can be illustrated with the help of the following experiments :

A drop of ink diffuses in water contained in a beaker till a homogeneous solution is formed. Two gases mix with each other when stopcock is opened. These processes proceed without exchange of energy or matter. But the process is always accompanied with an increase in entropy.

It may be concluded that **a spontaneous process in an isolated system is accompanied with an increase in entropy** or change in entropy is positive. However, for an open or close system, the change in entropy may be accounted in terms of the changes in the entropy of the system and the surroundings. The total entropy change (ΔS_{total})is then,

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \qquad ...(4.18)$$

For a spontaneous process, ΔS_{total} must be positive *i.e.*

$$\Delta S_{total} > 0 \qquad ...(4.19)$$

It is well established that the entropy of a system in equilibrium is maximum. The mathematical condition for entropy to be maximum is,

$$\Delta S = 0 \qquad ....(4.20)$$

Thus, for an equilibrium process change in entropy is zero. Let us consider the process, *e.g.*,

Ice → Water

The entropy values for water at different temperatures are given in **Table 4.3.**

We find that at 272 K, ΔS_{total} is positive, therefore, water will be frozen spontaneously. At 274K, ΔS_{total} is negative thus freezing is not spontaneous but the reverse change, *i.e.*, melting is spontaneous. At 273 K, ΔS_{total} is zero which means that neither the freezing

process nor melting process is spontaneous. At this temperature both water and ice are in equilibrium and no net change can be observed. Thus, we can state that $\triangle S_{total}$ is a criterion for spontaneity of a change.

Table 4.3. Entropy changes for the transformation HO(l)——HO(s) at 1 atm

Temperature °C	K	...S_{system} J/(K.mol)	...$S_{surroundings}$ J/(K.mol)	...S_{total} J/(K.mol)
−1	272	−21.85	+21.93	+0.08
0	273	−21.99	+21.99	0
+1	274	−22.13	+22.05	−0.08

4.7.2. Entropy Change in Phase Transformations. A solid is converted into liquid and liquid, in turn, is converted into gas. These changes take place at a fixed temperature and the two phases of the substance are in equilibrium with each other. The phase transformation processes may be represented as

$$\text{Ice (s)} \rightleftharpoons \text{Water (l)}$$
$$\text{Water (l)} \rightleftharpoons \text{Water (g)}$$
$$\text{Iodine (s)} \rightleftharpoons \text{Iodine (g)}$$

In phase transformation process, heat is absorbed or evolved at a fixed temperature. Melting of ice involves absorption of heat which is referred to as latent heat of fusion. Similarly, latent heat of vaporization is used up in the conversion of a liquid into a gas. The latent heat of phase transformation processes corrresponds to q_{rev} at constant pressure. The entropy of fusion is given by,

$$\triangle S_{fusion} = \frac{\Delta H_{fusion}}{T} \qquad \text{...(4.21)}$$

Similarly, if the latent heats of vaporization and sublimation are denoted by $\triangle H_{vap}$ and $\triangle H_{sub}$ respectively, entropies of vaporization and sublimation are given by the expressions,

$$\triangle S_{vap} = \frac{\triangle H_{vap}}{T} \qquad \text{...(4.22)}$$

and

$$\triangle S_{sub} = \frac{\triangle H_{sub}}{T} \qquad \text{...(4.23)}$$

4.7.3. Calculations of the Standard Entropy Change, $\triangle S°$, from the Tabulated Values of $S°$.

Table 4.4 gives the values of absolute entropy at 298K and 1 atm pressure. The change in entropy in a reaction, $\triangle S°$ is given by

$$\triangle S° = \Sigma S°_{(products)} - \Sigma S°_{(reactants)} \qquad \text{...(4.24)}$$

Table 4.4. Abso'u'e entropy at 298 K and 1 atmospheric pressure

Substance	S° (J K^{-1} mol^{-1})	Substance	S° (J K^{-1} mol^{-1})
$H_2(g)$	130.6	$HCl(g)$	186.7
$F_2(g)$	203.3	$HBr(g)$	198.5
$Cl_2(g)$	223.0	$HI(g)$	206.3
$Br_2(l)$	152.3	$NH_3(g)$	192.5
$I_2(s)$	116.7	$CH_4(g)$	186.2
$O(g)$	161.06	$C_2H_4(g)$	219.5
$O_2(g)$	205.03	( )	( )
$O_3(g)$	238.93	$C_2H_6(g)$	173.3
S(rhombic)	31.9	( )	( )
$N_2(g)$	191.5	$SO_2(g)$	248.5
C(graphite)	5.69	$CO_2(g)$	213.6
C(diamond)	2.4	$NO_2(g)$	240.5
Al(s)	28.3	$NaCl(s)$	72.38
$H_2O(g)$	188.7	$CaCO_3(s)$	92.9
$H_2O(l)$	69.96	$Al_2O_3(s)$	51.0
		$CO(g)$	197.6
		$HgO(s)$	72.0

(Note that the entropies of gases tend to be higher whereas those of solids are generally much lower.)

The entropy changes in the various reactions can be calculated with the help of values of absolute entropies given in the Table 4.4 and equation (4.24).

Exercise 4.13. *Calculate the standard entropy change for the reactions.*

(*i*) $2Al(s)+\frac{3}{2}O_2(g) \rightarrow Al_2O_3(s)$

(*ii*) $H_2(g)+Br_2(l) \rightarrow 2HBr(g)$

Solution. We use equation 4.24 and the data given in Table 4.4.

$$(i)\quad \Delta S^\circ_{reaction}=[S^\circ_{Al_2O_3(s)}]-[2\times S^\circ_{Al(s)}+\tfrac{3}{2}S^\circ_{O_2(g)}]$$
$$=[1 \text{ mol } 51{\cdot}0 \text{ JK}^{-1}\text{ mol}^{-1}]$$
$$-[2 \text{ mol } 28{\cdot}3 \text{ JK}^{-1}\text{ mol}^{-1}$$
$$+\tfrac{3}{2} \text{ mol } 205{\cdot}03 \text{ JK}^{-1}\text{ mol}^{-1}]$$
$$=(51{\cdot}0 \text{ JK}^{-1})-(56{\cdot}6+307{\cdot}9)$$
$$=-313{\cdot}5 \text{ JK}^{-1}$$

$$(ii)\quad \Delta S^\circ_{reaction}=[2\times S^\circ_{HBr(g)}]-[S^\circ_{H_2(g)}+S^\circ_{Br_2(g)}]$$
$$=2\,[\text{mol}\times 198{\cdot}5 \text{ JK}^{-1}\text{ mol}^{-1}]-[1 \text{ mol}\times 130{\cdot}6 \text{ JK}^{-1}\text{mol}^{-1}$$
$$+(1 \text{ mol}\times 152{\cdot}3 \text{ JK}^{-1}\text{ mol}^{-1})]$$
$$=(397{\cdot}0)-(130{\cdot}6+152{\cdot}3)\text{ JK}^{-1}=114{\cdot}1 \text{ JK}^{-1}$$

Exercise 4 14. (*i*) *Toluene* ($CH_3C_6H_5$) *has normal boiling point* 110·6°C *and standard enthalpies of vaporization,* $\Delta H°_{vap}$ 35·2 kJ mol^{-1}. *What is the entropy of vaporization of liquid toluene.*

(*ii*) *What is the entropy change for conversion of one mole of ice to water at 273* K *and 1* atm *pressure ?*

Solution. (*i*) Here $\Delta H°_{vap}=35200$ J mol^{-1}

$$T=110{\cdot}6+273{\cdot}2=383{\cdot}8 \text{ K}$$

Substituting the values in equation (4 22),

We have

$$\Delta S_{vap}=\frac{35200}{383{\cdot}8}=91{\cdot}7 \text{ JK}^{-1}\text{ mol}^{-1}$$

(*ii*) Since the system is at equilibrium $\Delta S=0$

Exercise 4.15. *Using values of absolute standard entropies at 298* K *given in Table 4.4, find the* $\Delta S°$ *for each of the following reactions* :

(*i*) $2O_3(g) \rightarrow 3O_2(g)$

(*ii*) $O_3(g) \rightarrow O_2(g)+O(g)$

Solution. (*i*) $\Delta S°_{(reaction)}=[3 \text{ mol} \times S_{O_2}(g) \text{ JK}^{-1} \text{ mol}^{-1}]$

$$[2 \text{ mol} \times S_{O_3}(g) \text{ JK}^{-1} \text{ mol}^{-1}]$$

$$=[3 \times 205{\cdot}03 \text{ JK}^{-1}]-[2 \times 238{\cdot}93 \text{ JK}^{-1}]$$

$$=137{\cdot}23 \text{ JK}^{-1}]$$

(*ii*) $\Delta S°(reaction)=[1 \text{ mol } S°O_2(g) \text{ JK}^{-1} \text{ mol}^{-1}+1 \text{ mol } S°O_2(g)$

$$\text{JK mol}^{-1}]-[1 \text{ mol } S° \; O_3(g) \text{ JK}^{-1} \text{ mol}^{-1}$$

$$=(205{\cdot}03 \text{ JK}^{-1}+161{\cdot}06 \text{ JK}^{-1})-(238{\cdot}93 \text{ JK}^{-1})$$

$$=127{\cdot}16 \text{ JK}^{-1}$$

4 8. GIBBS FREE ENERGY, G AND SPONTANEITY

We have seen that a spontaneous reaction is accompanied with decrease in enthalpy and increase in entropy. The total entropy change for a system and its surroundings is given by equation 4.18 *i.e.,*

$$\Delta S_{total}=\Delta S_{system}+\Delta S_{surroundings}$$

If a reaction is carried out at constant temperature and pressure and heat is given out to the surroundings, we can write

$$\Delta S_{surroundings}=\frac{-q_p}{T}=\frac{-\Delta H}{T} \qquad \ldots(4.25)$$

Substituting equation (4.25) in equation (4.18), we get

$$\Delta S_{total}=\Delta S_{system}-\frac{\Delta H}{T}$$

or
$$T\Delta S_{total}=T\Delta S-\Delta H \qquad \ldots(4.26)$$

All the terms on the right hand side in the equation (4.26) are the system properties so the subscript system has not been used. Equation (4·26) may be rearranged as follows :

$$-T\Delta S_{total}=\Delta H-T\Delta S \qquad ...(4{\cdot}27)$$

J.W. Gibbs studied the role of these concepts on the spontaneity of reactions. He introduced a new concept named as free energy and denoted by G. The free energy is also a state function and it is related with enthalpy and entropy using relation,

$$G=H-TS \qquad ...(4.28)$$

or

$$\Delta G=\Delta H-T\Delta S-S\Delta T \qquad ...(4.29)$$

G is a state function. At a constant temperature and pressure,

$$\Delta G=\Delta H-T\Delta S \qquad ...(4.30)$$

If we compare Equation (4.27) and (4.30) we find that,

$$\Delta G=-T\Delta S_{total} \qquad ...(4.31)$$

We know that for a spontaneous process, ΔS_{total} is always positive. The spontaneity of a process can be predicted in terms of free energy using equation (4.31).

Gibbs free energy has an advantage that it is related to the thermodynamic state functions of a system and does not take into account surroundings of the system. The second law of thermodynamics provides criteria of spontaneity in terms of total entropy change which includes system and the surroundings.

There can be three obvious possibilities on the basis of equation (4.30).

(*i*) **If ΔG is negative, the change is spontaneous.** Since ΔS_{total} is greater than zero for a spontaneous change, $T\Delta S_{total}$ must also be greater than zero and $-T\Delta S_{total}$ most be less than zero.

(*ii*) *If ΔG is zero, the system is in equilibrium.* We have seen that for a system in equilibrium $\Delta S_{total}=0$. It follows, therefore, that $\Delta G=0$ for an equilibrium state.

(*iii*) *If ΔG is positive, the change is non-spontaneous.* The reverse of the reaction, however, will be spontaneous.

The spontaneity of a chemical reaction is decided by two factors : (*i*) the energy factor, and (*ii*) the entropy factor. The equation, $\Delta G=\Delta H-T\Delta S$, takes both the factors into consideration. A reaction may have negative or positive values of entropy and enthalpy. But the spontanity can be predicted from the Table 4.5.

Table 4.5 Prediction of direction of reactions with different signs of ΔH and ΔS

ΔH	ΔS	ΔG	*Remarks*
−ve	+ve	−ve	Reaction will be spontaneous at all temperatures.
−ve	−ve	−ve if $\Delta H > T\Delta S$	(i) spontaneous at low temperatures. (ii) non-spontaneous at high temperatures.
+ve	+ve	−ve if $T\Delta S > \Delta H$	(i) spontaneous at high temperatures. (ii) non-spontaneous at low temperatures.
+ve	−ve	+ve	non-spontaneous at all temperatures.

The most favourable circumstances for a negative value of ΔG will be the a negative value of ΔH (lowering of enthalpy) together with a positive value of ΔS (increase of disorder).

Exercise 4.16. *For the reaction*

$$CCl_4(l)+H_2(g) \rightarrow HCl(g)+CHCl_3(l)$$

at 298 K $\Delta H^\circ = -91.34$ kJ *and* $\Delta S^\circ = 41.6$ JK^{-1}. *Find out if the above reaction is spontaneous at 298* K.

Solution. The ΔG° for the reaction can be calculated from the equation,

$$\Delta G^\circ = \Delta H - T\Delta S,$$

Substituting the values

$$\Delta G^\circ = -91.34 \times 10^3 \text{ J} - 298 \text{ K} \times 41.6 \text{ JK}^{-1}$$
$$= -103.68 \text{ kJ}$$

The negative value of ΔG° suggests that the reaction will be spontaneous at this temperature.

Exercise 4·17. *For the reaction*

$$Ag_2O(s) \rightarrow 2\,Ag(s) + \tfrac{1}{2}O_2(g)\ ;\ \Delta H^\circ = 30{\cdot}56 \text{ kJ mol}^{-1}$$

and $\Delta S^\circ = 0{\cdot}066$ kJ k^{-1} mol.

Calculate the temperature at which ΔG° *is equal to zero. Also predict the direction of reaction below this temperature.*

Solution. $\Delta G = \Delta H - T\Delta S$; when $\Delta G = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{30{\cdot}56 \times 10^3 \text{ J mol}^{-1}}{0{\cdot}066 \times 10^3 \text{ JK}^{-1} \text{ mol}^{-1}}$$
$$= 463 \text{ K or } 190^\circ\text{C}$$

KΔ, *i.e.*, ΔG° will be zero of 463 K.

or $\quad \Delta H = T\Delta S$

if temperature is less than 463 the $T\Delta S < \Delta H$; in that case ΔG is negative. The reaction will proceed in the forward direction spontaneously.

4.9. STANDARD FREE ENERGY CHANGE (ΔG°)

The standard free energy change is defined as the free energy change for a process at 298 K in which the reactants in their stan-

dard states are converted to the products in their standard states. It is denoted by the symbol $\Delta G°$.

Free energy change in a chemical reaction can be calculated using standard free energy of formation of the substances. The standard free energy of formation ($\Delta G_f°$) of a compound is defined as the change in free energy when 1 mole of the compound is formed from its constituent elements in their standard states. Like the standard enthalpy of formation of an element the standard free energy of formation of an element in its standard state is also zero.

$$\Delta G° = \Sigma \Delta G°_{(products)} \quad - \Sigma \Delta G°_{(reactants)} \quad ...(4.32)$$

= (sum of the standard free energies of formation of products) — (sum of the standard free energies of formation of reactants)

Some standard free energies of formation are given in Table 4.6.

Table 4.6 Standard Gibbs Free Energies of Formation ...G° at 298 K

Substance	ΔG (298) (kJ mol⁻¹)	*Substance*	ΔG_f(298) (kJ mol⁻¹)
		HI(g)	1.8
Al_2O_3(g)	—1576.41	N_2(g)	0.0
Br_2(g)	3.1	N(g)	455.6
Br(g)	82.4	N_2(g)	—16.6
Br(aq)	—102.8	NO(g)	86.7
G(graphite)	0.0	NO_2(g)	51.84
C(diamond)	2.8	NaCl(s)	—384.05
CH_4(g)	—50.8	O(g)	230.1
C_2H_4(g)	—32.9	O_3(g)	163.4
C_2H_2(g)	209.2	P(white)	0.0
C_6H_6(l)	124.5	P(red)	—12.0
CO(g)	—137.3	S(rhombic)	0.0
CO_2(g)	—394.4	SO_2(g)	—300.4
Cl(g)	105.4	H_2SO_4(l)	—690.0
Fe_2O_3(s)	748.0	SO_4^{2-} (aq)	—742.2
H(g)	203.3	H_2S(g)	—33.0
H_2O(l)	—237.2	ZnO(s)	—318.19
H_2O(g)	—228.6		
HCl(g)	—95.2		

Exercise 4.18. *Using the data from Table 4.6, calculate the $\Delta G_f°$ for the reaction,*

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

Solution. $\Delta G_f° = [2 \text{ mol } \Delta G°_{f\,HI(g)}] - [1 \text{ mol } \Delta G°_f H_2(g) + 1 \text{ mol } \Delta G°_f I_2(g)]$

or $=2\times1.8-(0+0)$
$=3.6$ kJ mol^{-1}

4.10. STANDARD FREE ENERGY CHANGE AND EQUILIBRIUM CONSTANT. The standard free energy change, ΔG° is related to the equilibrium constant K by the relation

$$\Delta G^\circ = -2{\cdot}303\ RT \log K \qquad ...(4.33)$$

This equation helps us to determine the value of ΔG° if K is known or vice versa.

Exercise 4·19. *Calculate the free energy change for the following reaction :* $CH_3COOH(l)+C_2H_5OH(l) \rightarrow CH_3COOC_2H_5(l)+H_2O(l)$ *at 298 K,*

K (the equilibrium constant) [equal to 4.]

Solution. We know, $\Delta G=2.303\ RT\log K$, substituting the values,

$$\Delta G = -2.303\ RT \log 4$$
$$= -2.303\times8.31\ \text{JK}^{-1}\times298\ \text{K}\log 4$$
$$= -3473\ \text{J mol}^{-1} = -3.473\ \text{kJ mol}^{-1}$$

4.11. GIBBS FREE ENERGY AND WORK. When heat is supplied to a gas at constant pressure, the gas expands. In doing so, it does some work against the external pressure. If we consider a gas cylinder fitted with a piston, the supply of heat to the gas will be used up

(*i*) to increase the internal energy of gas

(*ii*) to expand the gas

(*iii*) to do some work on the piston so that it moves to a new position of equilibrium.

In a reversible cyclic process, useful work can be obtained from a gas which can be related with free energy change as

$$\Delta G = -W_{max}$$

Thus, spontaneous process will always perform some work. The greater the free energy change, the greater is the amount of work that can be obtained from the process. Now, we can say that ΔG can be used to have two vital informations about the chemical or physical changes :

(*i*) spontaneity of the process

(*ii*) useful work obtainable from the process.

It can be shown that free energy for a process is equal to the maximum possible work that can be derived from the process.

In a galvanic cell (which you will study in Unit 5), free energy change ΔG, is related to the electrical work done in the cell. If E is the e.m.f. of the cell and n moles of electrons are involved, the electrical work will be equal to nFE (where is F the Faraday constant). Thus,

When the $\Delta G = -nFE_{cell}$ (4.34)

If reactants and products are in their standard states,

$$\Delta^{\circ}G = -nFE^{\circ}_{cell} \quad (4.35)$$

Here E°_{cell} is the standard cell potential.

4.12. ABSOLUTE ENTROPIES AND THIRD LAW OF THERMODYNAMICS

Experiments showed that as temperature decreases, ΔG of a process approches ΔH more closely as shown in Fig. 4 10. This is due

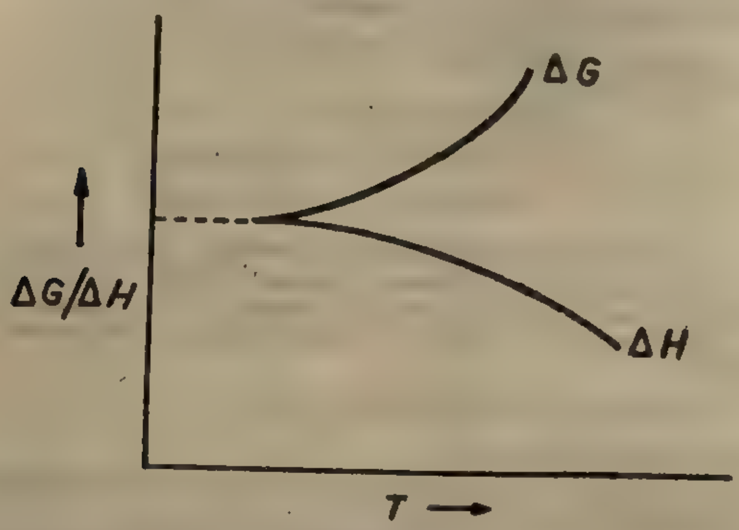


Fig. 4.10.

to the fact that entropy of a pure substance increases with increase in temperature. A solid melts and then vaporizes if we go on increasing the temperature of the solid. Conversely, the entropy of a substance must decrease with decrease in temperature. Nernst (1906) proposed the third law of thermodynamics, according to which the **entropy of a perfectly crystalline substance at 0°K is taken as zero.** The third law may be defined in several forms, *e.g.*,

(*i*) **It is impossible to attain absolute zero in a finite number of operations.**

(*ii*) **No system can be reduced to 0°K.**

The third law of thermodynamics provides a method to calculate the absolute value of entropies of any pure substance at any temperature.

Exercise 4.20. *A gas having an initial volume of 50·0 m³ at an initial pressure of 2·0 × 10⁵ Pa is allowed to expand against opposing pressure of 1·0 × 10⁵ Pa. Calculate the work done by the gas. If the gas is ideal and the expansion is isothermal, what is q for the gas?*

Solution. Initial pressure of the gas $=2.0\times10^5$ Pa

Initial volume of the gas $=50.0\ m^3$

Final pressure of the gas $=1.0\times10^5$ Pa

Final volume of the gas $=100.0\ m^3$ $\quad (\because\ P_1V_1=P_2V_2)$.

Here the change in the volume, ΔV of the gas $=100{\cdot}0-50{\cdot}0=50.0\ m^3$. This expansion of the gas takes place against the pressure 1.0×10^5 Pa.

Therefore, work done, $w=P\Delta V$

$$=1.0\times10^5\ N\ m^{-2}\times50.0\ m^3$$
$$=5.0\times10^6\ J=5.0\times10^3\ kJ$$

As work is done by the system, it will have negative sign. Thus, work done in the expansion of the gas $=-5.0\times10^3$ kJ

We know

$$\Delta E=q+w \quad \text{when } \Delta E=0$$

or $$q=-w$$

or $$q=-(-5.0\times10^3\ kJ)=5.0\times10^3\ kJ$$

Exercise 4.21. *The heat of vaporization, $\Delta H vap$ of H_2O at 298 K is 44.0 kJ mol⁻¹. Calculate q, w and ΔE for the process.*

Solution. The heat absorbed at constant pressure.

$$q_p=\Delta H_{vap}=44.0\ kJ\ mol^{-1}$$

Calculation of w,

$$H_2O(l)=H_2O(g)$$

here $$\Delta n=1-0=1$$

work $$w=\Delta nRT$$
$$=1.0\times8.31\times298=2476kJ$$
$$=2.48\ kJ$$

We know

$$\Delta H=\Delta E+\Delta n\ RT$$

or $$44.0\ kJ=\Delta E+2{\cdot}48\ kJ$$

or $$\Delta E=41.52\ kJ\ mol^{-1}$$

Exercise 4.22. At *0°C ice and water are in equilibrium and* ΔH is 6.00 kJ mol⁻¹ *for the process*

$$H_2O(s)\longrightarrow H_2O(l)$$

Calculate ΔS for the conversion of ice to water.

Solution. $\Delta S = \frac{\Delta H}{T}$

$= \frac{6.0 \times 10^3 \text{ J}}{298 \text{ K}} = 20.0 \text{ Jk}^{-1}$

Exercise 4.23. *For a reaction,* $\Delta H = -11.7$ Jk mol^{-1},

and, $\Delta S = -105$ Jk^{-1} mol^{-1}

Predict if this reaction will be spontaneous at 298 K.

Solution. $\Delta G = \Delta H - T\Delta S$

or $\Delta G = -11.7 \times 10^3 \text{ J} - 298 \times (-105)$

$= -11700 + 31290$

$= 19590 \text{ J mol}^{-1}$.

As ΔG is positive, the reaction will not be spontaneous.

Exercise 4.24. *Calculate* $\Delta G°$ *for the reaction at 298 K*

$PCl_5 \text{ (g)} \rightleftharpoons PCl_3 \text{ (g)} + Cl_2 \text{ (g)}$

at 298 k, $K = 1.8 \times 10^{-7}$,

Solution. $\Delta G° = -2.303 \, RT \log K$

$= -2.303 \times 8.31 \text{ J} \times 298 \log 1.8 \times 10^{-7}$

$= -2.303 \times 8.31 \text{ J} \times 298 \times (-6.7447)$

38466 J mol^{-1} = 38.47 kJ mol^{-1}

Exercise 4.25. *For the reaction,*

$2NO_2 \text{ (g)} \rightleftharpoons N_2O_4\text{(g)}$

$\Delta G° = -4.73$ kJ *at 298* K.

Calculate the value of K *at 298* K *for this reaction.*

Solution. $\Delta G° = -2.303 \, RT \log K$

or $\log K = \frac{\Delta G°}{-2.303 \, RT}$

$= -\frac{4.73 \times 10^3 \text{ J}}{(-)2.303 \times 8.31 \text{ J} \times 298}$

$= 0.8294$

Taking the antilog, $K = 6.76$

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

4.1 **Choose the correct of the four alternatives given for the following questions :**

(*i*) Which of the following is an intensive property ?
(*a*) energy (*b*) enthalpy (*c*) kinetic energy (*d*) temperature

(*ii*) One litre atmosphere equals
(*a*) 4.81 joules (*b*) 8.31 joules (*c*) 19.12 joules (*d*) 101.3 joules

(*iii*) For which of the following process ΔE of the system increases ?
(*a*) $H_2(g)+I_2(g) \rightarrow 2HI(g)$
(*b*) Decrease in temperature of the system by 10°C
(*c*) $q<0$ and $w<0$
(*d*) $q=0$ and $w>0$

(*iv*) A system performs 410L atm pressure–volume work (1L atm= 101.3J) on its surroundings and absorbs 2000J of heat from the surroundings. The change in internal energy of the system is
(*a*) 43530 J (*b*) 39530 J (*c*) −39530 J (*d*) −2000 J

(*v*) At constant pressure q equals
(*a*) ΔE (*b*) ΔH (*c*) $P\Delta V$ (*d*) ΔS

(*vi*) For an adiabatic process
(*a*) $\Delta E=q$ (*b*) $P\Delta V=0$ (*c*) $q=0$ (*d*) $\Delta S=0$

(*vii*) ΔG for a reaction equals to zero, if
(*a*) the system is at equilibrium (*b*) no heat is evolved
(*c*) no heat is absorbed (*d*) $\Delta S=0$

(*viii*) Which of the following is an incorrect statement ?
(*a*) The energy of the universe is constant.
(*b*) The entropy of the universe is constant.
(*c*) Energy of products is more than that of reactants in an endothermic reaction.
(*d*) The state of maximum entropy is the most stable state for an isolated system.

(*ix*) If an endothermic reaction occurs spontaneously at constant temperature T and P, then the............ must be true :
(*a*) $\Delta G>0$ (*b*) $\Delta H<0$ (*c*) $\Delta S>0$ (*d*) $\Delta S<0$

(*x*) At a given temperature the value of the equilibrium constant for a reaction can be calculated from the balanced equation and
(*a*) ΔG (*b*) ΔG (*c*) ΔH (*d*) $T\Delta S$

4.2 **Fill in the blanks :**

(*i*) The system absorbs heat......the surroundings is an......process.

(*ii*) The increase in internal energy of a system equals the heat exchanged by the system plus......the system.

(*iii*) In the reaction

$$H^+(aq)+OH^-(aq) \rightarrow H_2O\,(l)$$

the work is......

(*iv*) Bomb calorimeter measures heat of a reaction at constant......

(v) Hess's law of heat summation is a direct consequence of the.........

(vi) Heat of formation of $O_2(g)$ at 298 K and 101,325 Pa pressure is equal to.........

(vii) $\Delta G^\circ = \Delta H^\circ$.........

(viii) $\Delta G^\circ = -2.303$......

(ix) A reaction for which $\Delta G^\circ > 0$ and $K < 1$ will be.........in forward direction.

(x) Dissolving sugar in water.......entropy.

4.3 Point out the true (T) or false (F) statements of the following :

(i) More heat is evolved in the combustion of 1 mole of carbon than in the combustion of 28g of CO.

(ii) It is immaterial whether the standard enthalpy of combustion of sulphur is found at constant volume or constant pressure.

(iii) Gain of information is loss of entropy.

(iv) When $CaCO_3(s)$ is heated to form $CaO(s)$ and CO_2 gas. The entropy of the system increases.

(v) All natural processes in which heat is transferred eventually reach an equilibrium temperature at which the ΔS is equal to zero.

(vi) When a liquid boils there is an increase in enthalpy.

(vii) Energy can be transferred as heat or work.

(viii) It is found that at a given temperature $\Delta G = -41.0$ kJ/mol for the reaction

$$C(s) + O_2(g) = CO_2(g)$$

at this temperature and, the system is at equilibrium for the reaction.

(ix) According to the third law of thermodynamics, S=0 for a perfect crystal at 0°C.

(x) $\Delta G^\circ = nFE^\circ$.

4.4 Match the following choosing one item from Column X and the appropriate item from Column Y

Column X	Column Y
(A) ΔH is negative	(i) ΔnRT
(B) Δn_{gas} = zero	(ii) equilibrium state
(C) $(\Delta G)P,T$	(iii) $\Delta T = 0$
(D) Pressure-volume work	(iv) $N_2(g) + O_2(g) \rightarrow 2NO(g)$
(E) $\Delta G^\circ = 0$	(v) crystallization of sugar
(F) ΔS is negative	(vi) exothermic process
(G) Isothermal change	(vii) $N_2(g)$
(H) $(\Delta G)_{T,P} < 0$	(viii) $H - T\Delta S$
(I) $\dfrac{\Delta H_{vap}}{\Delta S_{vap}}$	(ix) spontaneous reaction
(J) ΔH°_f = zero	(x) boiling point

SHORT ANSWER QUESTIONS

4.5 The reaction $X \longrightarrow Y$ is exothermic. Is the enthalpy of Y greater or less than that of X ? Why ?

4.6 State whether each of the following will increase or decrease the total energy content of the system :

(a) Heat transferred to the surroundings

(b) Work done by the system

(c) Work done on the system

4.7 What will be the sign of ΔG for melting of ice at

(a) 273.15 K and (b) 265 K

4.8 Determine the sign of the entropy change in the following reactions :

(i) $NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(l)$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

(iii) $C(graphite) + CO_2(g) \longrightarrow 2CO(g)$

(iv) $AgNO_3(aq) + NaCl(aq) \longrightarrow NaNO_3(aq) + AgCl(s)$

4.9 At temperature, T the endothermic reaction $A \rightarrow B$ proceeds almost to completion. What would be the sign of ΔS at the temperature T ?

4.10 In which of the following cases a reaction is possible at all the temperature :

(a) $\Delta H^\circ < 0$; $\Delta S^\circ > 0$

(b) $\Delta H^\circ > 0$; $\Delta S^\circ > 0$

4.11 Why is ΔE equal to zero for an isothermal expansion of an ideal gas ?

4.12 Why is it not possible to measure or calculate E for a system ?

4.13 Taking into account that $NO_2(g)$ is coloured and $N_2O_4(g)$ is colourless, and proceeding from the sign of the change in the entropy in the reaction $2NO_2(g) = N_2O_4(g)$, predict how the colour will change in the system $NO_2 - N_2O_4$ with increase of the temperature.

4.14 What is the relationship between the enthalpy and the entropy changes for a process at equilibrium.

TERMINAL QUESTIONS

4.1 Define the following terms : (i) Isolated system, (ii) State variables, (iii) Adiabatic expansion, (iv) Extensive property, (v) Standard enthalpy of formation of a substance, (vi) Entropy, (vii) Surroundings, (viii) Reversible process, (ix) Internal energy and (x) Standard free energy change.

4.2 State the first law of thermodynamics.

4.3 Why is ΔE called the heat of reaction at constant volume ? Why is ΔH called the heat of reaction at constant pressure ?

4.4 What is the third law of thermodynamics ?

4.5 Correlate entropy and disorder using fusion and vaporization.

4.6 For the reaction.

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$$

Calculate ΔH and ΔE at 298 K and 1 atm pressure. Take heat of formation of the compounds from Table 4·1.

(Ans. $\Delta H = -1411$ kJ ; $\Delta E = -1406$ kJ)

4.7 Calculate ΔH for the ionization of HBr.

$$HBr(g) \longrightarrow H^+(aq) + Br^-(aq)$$

if heat of formation for HBr(g), $H^+(aq)$ ann $Br^-(aq)$ are —36·23, 0.0 and —121·0 kJ mol^{-1} respectively.

(Ans. $\Delta H = -84.77$ kJ)

4.8 Using bond energies from Table 4.2 estimate the heat of formation of HF(g). (Ans. $\Delta H_f(g) = -269.5$ kJ mol^{-1})

4.9 When 1.0 mole of molecules of a gas is compressed. the work done is 200 J. The heat energy then evolved is 300 J. Calculate ΔE of the gas. (Ans. $\Delta E = -20$ J)

4.10 The normal boiling point of sodium is 810°C and the heat of vaporization is 70.18 kJ mol^{-1}. Calculate $\Delta S°$ for the condensation of sodium vapour. Is this an increase or decrease in entropy for sodium ?

(Ans. $\Delta S = -64.8$ JK^{-1} mol^{-1}, decrease)

4.11 Using the absolute entropies given in Table 4.4 determine entropy change for the following reaction :

$$N_2(g) + 2O_2(g) \longrightarrow 2NO^-(g)$$

(Ans. $\Delta S = -220{\cdot}56$ JK^{-1})

4.12 Calculate $\Delta G°$ at 400 K for the reaction

$$BeSO_4(s) \longrightarrow BeO(s) + SO_3(g) \quad K_p = 3.87 \times 10^{-16} \text{ at } 400K$$

(Ans. $\Delta G° = 118$ kJ mol^{-1})

ANSWERS TO SELF ASSESSMENT QUESTIONS

4.1 (*i*) (d) (*ii*) (d) (*iii*) (d) (*iv*) (c) (*v*) (b) (*vi*) (c) (*vii*) (a) (*viii*) (b) (*ix*) (c) (*x*) (a)

4.2 (*i*) absorbs, exothermic (*ii*) work done on or by (*iii*) negligible (*iv*) volume (*v*) first law of thermodyamics. (*vi*) zero (*vii*) $-T\Delta S°$ (*viii*) *RT log K* (*ix*) non-spontaneous (*x*) increases

4.3 (*i*) T (*ii*) T (*iii*) T (*iv*) T (*v*) F (*vi*) T (*vii*) T (*viii*) F (*ix*) F (*x*) F

4.4 (A) (*vi*) ; (B) (*iv*) ; (C) (*viii*) ; (D) (*i*) ; (E) (*ii*) ; (F) (*v*) ; (G) (*iii*) ; (H) (*ix*) ; (I) (*x*) ; (J) (*vii*)

4.5 The enthalpy of Y is less than that of X because in the process some heat is transferred to the surroundings.

4.6 (*a*) and (*b*) will decrease whereas (*c*) will increase the total energy content of the system.

4.7 (*a*) zero, because the system is at equilibrium.
(*b*) positive, reaction being non-spontaneous.

4.8 (*i*) One mole of a substance in the solid state forms 1 mole gaseous product and 2 moles liquid product, hence ΔS is positive.
(*ii*) 1·5 moles of gaseous reactants get converted into 1 mole liquid product, ΔS is negative.
(*iii*) There is an increase in the number of gaseous molecules in the reaction, ΔS is positive.
(*iv*) More order, ΔS is negative.

4.9 The reaction is endothermic and proceeds to almost completion, hence ΔH is positive, ΔG is negative.
$\Delta G = \Delta H - T\Delta S$. To have ΔG negative, ΔS should be positive

4.10 $\Delta G = \Delta H - T\Delta S$
(*a*) Here ΔH is negative and ΔS positive thus ΔG will be negative at all the temperatures. Thus reaction (*i*) will proceed at any temperature

(b) Since ΔH is positive, ΔG may be positive; all negative will depend on the values of ΔH, T and ΔS. Thus, this reaction will not take place at all the temperatures.

4.11 When the temperature is constant during expansion or compression, the average kinetic energy of the molecules remains unchanged. For an ideal gas there is no molecular attraction, hence there is not change in its potential energy also. Therefore, in such a case $\Delta E=0$.

4.12 The internal energy is the total energy of a system that it possesses as a consequence of the kinetic energy of its atoms, ions, or molecules plus all the potential energy that arises from the binding forces between the particles making up the system. We can neither determine the absolute values of these factors since we do not know how fast the system or its particles are moving nor we can measure all the attractive repulsive forces present in the system.

4.13 Increase in temperature would result increase in the entropy as one mole of N_2O_4 on decomposition gives NO_2, i.e.,

$$N_2O_4 \rightarrow 2NO_2$$

Increase in temperature, therefore, will make it dense and coloured.

4.14 We know, $\quad \Delta G=\Delta H-T\Delta S$

At equilibrium $\Delta G=0$

or $\quad \Delta H=T\Delta S$

□□

UNIT 5
Electrochemistry

Davy supposes that there are two kinds of electricity, with one or other of which all bodies are united. These we distinguish by the names of positive and negative electricity.... But whether the hypothesis be altogether founded on truth or not, it is impossible to question the great influence of electricity in chemical combinations.

—JANEK MARCET

UNIT PREVIEW

5.1 Introduction.

5.2 Electrolytic conductance : molar conductivity and its variation with concentration.

5.3 Electrolytic cells—Faradays laws.

5.4 Voltaic or galvanic cells.

5.5 Electrode potential and electromotive force : standard electrode potential and its measurement, dependence of emf. on concentration and temperature.

5.6 Gibb's free energy and cell potential.

5.7 Electrode potential and electrolysis.

5.8 Some commercial cells (batteries) and fuel cell.

5.9 Corrosion

Self assessment questions

Terminal questions

Answers to self assessment questions,

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Understand the origin of electrolytic conduction and the factors that affect conductance.
2. Describe a voltaic cell as composed of an oxidation and a reduction half reactions.
3. Sketch the voltaic cells to show that the anode and cathode, the half-cell reactions and the direction of electron and ion flow.
4. Describe the electrode potentials and cell potentials.

Define the standard electrode potential.

Relate the emf of a cell to the difference between the potentials of the two half-cells and explain that the standard E° is the potential occurring when all reactants are in their standard states and the cell is operating reversibly.

Calculate the cell potentials from electrode potential.

8. Explain that the spontaneous reaction occurring in a voltaic cell is accompanied by a decrease in Gibb's free energy.
9. Relate emf of the cell with Gibb's free energy of the cell reaction.
10. Interconvert $E°$, $\Delta G°$ and K_c.
11. Correlate the effects of concentration changes on cell potentials.
12. Calculate the cell and electrode potentials under non-standard conditions using the Nernst equation.
13. Describe the common types of commercial cells and fuel cell.
14. Explain electrolysis as a reversal of the operation of galvanic cell.
15. Describe the electrochemical basis of corrosion and suggest measures for preventing corrosion.

5.1. INTRODUCTION

Chemical reactions are a source of energy as the elements tend to gain or lose electrons in the drive towards stability. From the knowledge and understanding of the electron exchange process we learn how chemical energy is converted into electrical energy in electrochemical cells. Chemical reactions are spontaneous (occur naturally without external help or stimulus) in one direction because the reactants are at a higher potential energy state (in the form of chemical energy) than the products. When the reaction proceeds, the difference in chemical energy between the reactants and the products can be liberated as heat energy or converted to electrical energy. It is also possible to convert electrical energy into chemical energy as matter is composed of electrically charged particles. The study of these interconversions processes is an important part of electrochemistry, which is primarily concerned with the relationship between electrical energy and chemical energy. The spontaneous generation of electrical energy involves the use of redox reactions. Electric current can be conducted through pure liquid electrolytes or solutions containing electrolytes. This type of conduction is called ionic or electrolytic conduction. This involves the conduction of electric current by the motion of ions, both positive and negative, toward the electrodes through a solution or a pure liquid.

The electron flow which constitutes the current in the external circuit is set up under the influence of electromotive force of the cell.

5.2. ELECTROLYTIC CONDUCTANCE

The mobility of electrons through the metallic lattice of metals make them good conductors of electricity. Metals offer some resistance to the flow of an electric current. Solutions of electrolytes have a much higher resistance than metallic conductors. So the electrolytic conduction depends upon the free movement of ions through solution. The factors which affect the electrical conductivity of solutions of electrolytes are :

—the interionic attraction
—the solvation of ions
—the viscosity of the solvent

The resistance offered to the flow of current by the solutions of electrolytes generally decreases as the temperature rises. Like all electrical conductors, ionic solutions obey Ohm's Law, that is to say the current I, flowing through a solution of resistance, R is related to the potential difference, V by

$$V = IR \qquad \text{...(5.1)}$$

As for other conductors, the resistance of a conducting solution is directly proportional to its length (l), but inversely to its area of cross-section (A), *i.e.*,

$$R \propto \frac{l}{A}$$

or

$$R = \frac{\rho l}{A} \qquad \text{...(5.2)}$$

ρ is the proportionality constant and is called the **resistivity (specific resistance)**. Its units are Ω m (or Ω cm). Physically, resistivity is the resistance of one metre cube of the conductor, since $\rho = R$ when $l = 1$ m and $A = 1$ m².

Conductance (G) is the reciprocal of resistance, *i.e.*, R^{-1}. Its units are therefore Ω^{-1} (ohm), known as siemens (S). The reciprocal of resistivity of a solution is called its electrolytic conductivity (or specific conductivity). This is normally given a symbol κ (kappa) a Greek letter.

Thus,

$$\kappa = \frac{1}{\rho} \qquad \text{...(5.3)}$$

Substituting the value of ρ from equation (5·2), we get

$$\kappa = \frac{l}{RA} \qquad \text{...(5.4)}$$

Equation (5.4) shows that the units of κ are S m/m², *i.e.* S m^{-1} (or S cm^{-1}). Here $\left(\frac{l}{A}\right)$ is a fixed quantity for a cell and is called cell constant. The physical significance of κ can be understood by taking $l = 1$ m and $A = 1$ m², in which case $\kappa = G =$ the conductance of one metre cube of the solution. Because $\left(\frac{l}{A}\right)$ is constant, it forms the basis for comparisons of the conducting powers of different solutions.

Conductivities of some substances are given in Table 5.1.

TABLE 5.1. Conductivity of substances at room temperature

Substance	κ ohm^{-1} cm^{-1}	*Substance*	κ ohm^{-1} cm^{-1}
0·1 M HCl	3.5×10^{-2}	Silver metal	5.0×10^{5}
0·1 M NaCl	9.2×10^{-3}	Iron metal	1.0×10^{5}
0·01 M NaCl	1.2×10^{-3}	Graphite	1.2×10^{3}
0·1 M CH_3COOH	4.7×10^{-4}	Glass	1.0×10^{-14}
0·01 M CH_3COOH	1.6×10^{-4}	Teflon	1.0×10^{-18}
Water (very pure)	6.0×10^{-8}		

The expression for the electrolytic conductivity involves the distance (l) between the electrodes and the cross-sectional area of the conducting part of the solution (A), both of which are difficult to measure directly. This is performed by the determination of the conductance of a solution of known specific conductance, usually potassium chloride solution (Table 5 2). The conductance of the solution measures the conductance of the cell. This gives the factor by which the conductance of the solution in the cell must be multiplied to get the conductivity and is known as the cell constant $\left(\frac{l}{A}\right)$

TABLE 5.2. Specific conductance of KCl solution (aq)

Concentration mol dm^{-3}	*Specific conductance* ohm^{-1} m^{-1}
1.00	11.17 (298 K)
1.00	9.78 (291 K)
1.00	6.51 (273 K)
0.10	1.29 (298 K)
0.010	0.14 (298 K)
0.001	0.015 (298 K)

Exercise 5.1. *The resistance of a cell containing 0.010* M *KCl solution is found to be 1223* ohm *at 298* K. *The same cell has a resistance of 4546* ohm *when it contains a 0.05* M *ethanoic acid solution at 298* K. *Calculate the specific conductance of ethanoic acid. (Specific conductance of 0.01* M *KCl solution is 0.14* ohm^{-1}m^{-1} *at 298* K).

Solution : We know

$$\frac{l}{A} = \kappa \times R$$

$$= 0.14 \times 1223 = 171.22$$

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

(ethanoic acid)

$$= \frac{1}{4546} \times 171.22 \text{ ohm}^{-1} \text{ m}^{-1}$$
$$= 3.76 \times 10^{-2} \text{ ohm}^{-1} \text{ m}^{-1}$$

5.2.1. Measurement of conductance

The basic circuitry for a conductance cell is a wheatstone bridge (Fig. 5.1). The bridge differs from the usual type in that it uses alternating current rather than direct current; the latter would cause electrolysis and so alter the concentration of the solution. It is likely that during electrolysis, if direct current is used, certain gases are evolved. The gases adhere to the electrodes forming a gaseous layer which is a poor electrical conductor. As a result, the current drops and so the applied potential has to be increased in order that the cell reaction may continue. This effect is known as **polarisation.**

With the conductivity cell in position, the resistances R_1, R_2 and R_3 are adjusted until no current flows through the detector (includes earphones, an oscilloscope, a magic eye device *etc.*). At the balance point (as indicated by the detector), the resistance of the cell is given by

$$\frac{R_{\text{cell}}}{R_1} = \frac{R_3}{R_2}$$

or
$$R_{\text{cell}} = R_1 \cdot \frac{R_3}{R_2} \qquad \text{...(5.5)}$$

A typical conductivity cell is shown in Fig. 5.2. The cell is made of glass which consists of two parallel platinum electrodes covered with platinum black (minimises polarisation effects).

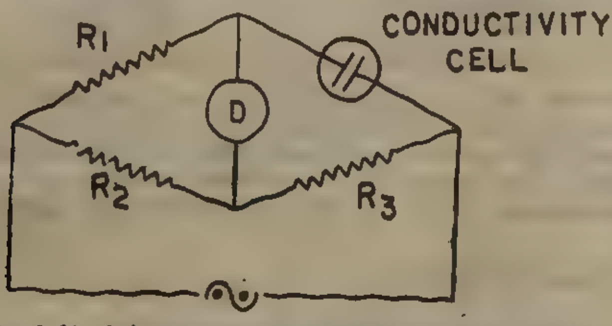


Fig. 5.1. Experimental set up for measuring electrolytic conductivity

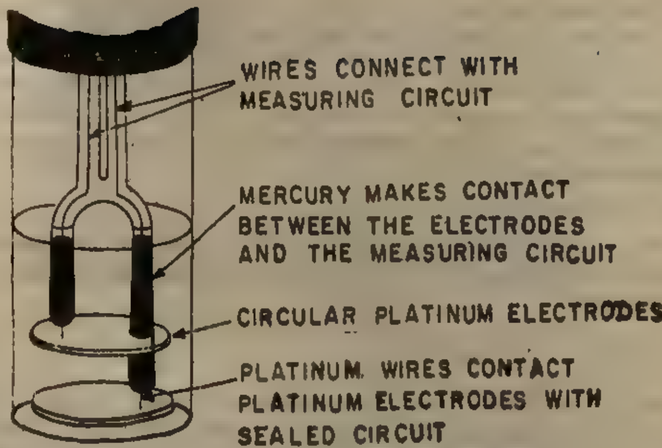


Fig. 5.2. A conductivity cell

Once the resistance of the cell has been measured, the specific conductivity of the solution is found from equation (5.4).

$$\kappa = \frac{l}{AR}$$

The cell constant $\left(\frac{l}{A}\right)$ is determined at the observed temperature before using the cell by using standard KCl solution.

From Table 5.2, it is clear that the conductance varies with concentration. A graph given in Fig. 5.3 suggests two counteracting effects :

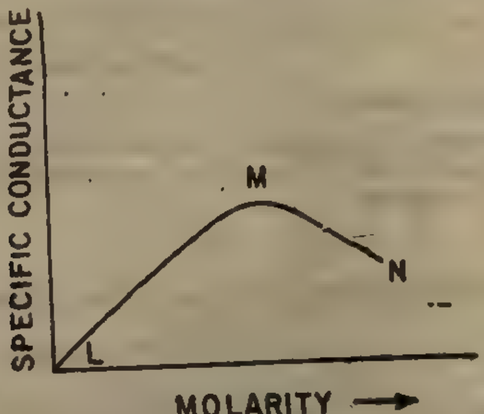


Fig. 5.3. Conductance curve

(*i*) an increase in the number of molecules increases the number of ions, *i.e.*, the conducting ions (suggested through LM portion of the curve), and (*ii*) a decrease in the degree of ionization because of the availability of lesser number of solvent molecules for ion formation (suggested through MN portion of the curve). These effects suggest the introduction of an additional term, *i.e.*, **molar conductance** (Λ_m).

Molar Conductance

This is defined as the conductivity (specific conductance) divided by the concentration of the solution expressed in mol L^{-1} (or mol dm^{-3}),

$$\Lambda_m = \frac{\kappa}{C} \quad \text{...(5.6)}$$

If k is in $\Omega^{-1}\ cm^{-1}$ and c is in mol dm^{-3}, then $\Lambda_m = \Omega^{-1}\ cm^2\ mol^{-1}$, and Λ_m is numerically equal to the conductivity of 1 mole of the electrolyte. It may thus be defined as the conductance between electrodes 1 cm (or 1 m) apart, of that volume of solution that contains 1 mol of solute.

that is $$\Lambda_m = \frac{1000 \times \kappa}{cM} \quad \text{...(5.7)}$$

Exercise 5.2. *Calculate the molar conductivity of sodium chloride of conductivity of* 0·100 mol dm^{-3}, *given that its conductivity is* 3.91 $\Omega^{-1}\ m^{-1}$.

Solution : We know $\Lambda_m = \frac{\kappa}{c}$

$$c = 0.100 \text{ mol dm}^{-3} = 100 \text{ mol m}^{-3}$$
$$\kappa = 3.91\ \Omega^{-1}\ m^{-1}$$
$$\Lambda_m = \frac{3.91\ \Omega^{-1}\ m^{-1}}{100 \text{ mol m}^{-3}} = 3.91 \times 10^{-2}\ \Omega^{-1}\ m^2\ mol^{-1}$$
$$= 391\ \Omega^{-1}\ cm^2\ mol^{-1}$$

Equivalent Conductance

It is convenient to compare quantitatively the conductivities of electrolytes in terms of equivalent conductance (Λ_{eq}) which is defined by the equation

$$\Lambda_{eq} = \frac{\kappa}{c} \quad \text{...(5.8)}$$

where c is the concentration of the solution in equivalents per litre.

Also $$\Lambda_{eq} = \frac{\kappa \times 1000}{N} \ (N = \text{normality}) \quad \text{...(5.9)}$$

Exercise 5.3. *The resistance of* $\frac{M}{10}$ *solution of NaOH solution offered a resistance of* $2{\cdot}5 \times 10^{2}$ ohm *in a conductivity cell at*

298 κ. Calculate the molar conductivity and equivalent conductivity of $\frac{M}{10}$ *NaOH solution. The cell constant is 1.150* cm^{-1}.

Solution :

Specific conductivity $\kappa = \dfrac{\text{cell constant}}{R}$

$$= \frac{1.15\ cm^{-1}}{2.5 \times 10^{3}\ ohm}$$

$$= 4.6 \times 10^{-4}\ ohm^{-1}\ cm^{-1}$$

Molar conductivity ; $\Lambda_m = \dfrac{1000 \times \kappa}{M}$

$$= \frac{1000\ cm^{3} \times 4.6 \times 10^{-4}\ ohm^{-1}\ cm^{-1}}{0.1}$$

$$= 4.6\ ohm^{-1}\ cm^{2}$$

Equivalent conductivity or molar conductivity of NaOH will be the same because the molar mass and the equivalent mass of NaOH are the same.

5.2.2. Variation of molar conductivity with concentration (or dilution)

The term dilution refers to the number of litres of solution which contain a fixed amount of electrolyte say 1 mole. When values of molar conductivity, Λ_m are plotted against the volume of solution containing 1 mole of solute the curves obtained for different electrolytes fall into two categories (Fig. 5.4).

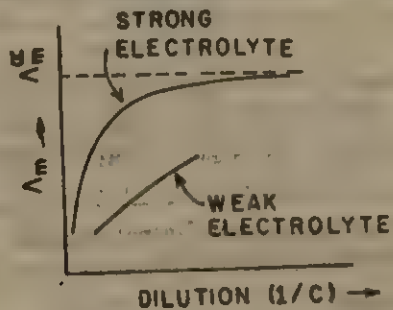


Fig. 5·4. Variation of molar conductivity with dilution

Provided the number of ions formed by the electrolyte remains constant, a simple calculation will show that the value of the molar conductivity of a solution should be independent of dilution (or concentration). In reality the situation is very different (Figs. 5.4 and 5.5).

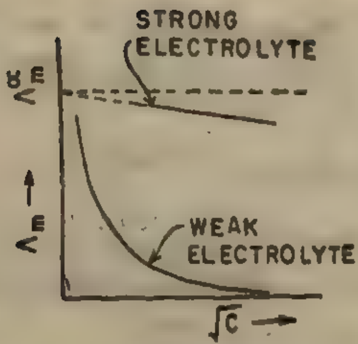


Fig. 5·5. Variation of molar conductivity with concentration

For KCl, the molar conductivity has a fairly high value even in concentrated solution; it increases rapidly at first and then levels off. The maximum value is obtained at high dilution and is known as the molar conductivity at infinite dilution, represented as Λ_m^{∞}. For acetic acid, the molar conductivity has a low initial value in concentrated solution, and it increases slowly as the solution becomes more and more dilute. The values of molar conductivities for KCl and acetic acid at the various dilutions are given in Table 5·3. From the table it is evident, that the value of molar conductivity of acetic acid at infinite dilution is very much higher than that of potassium chloride.

TABLE 5.3. Molar conductivities (ohm^{-1} cm^2) at different dilution

Dilution	*1*	*10*	*100*	*1000*	*5000*	*10000*	∞
Λ_m (KCl)	98.3	112	122	127	128	129	130
Λ_m (acetic acid)	1·3	4·6	14·3	41	50	107	350

To understand the reasons for variation of Λ_m with concentration we must consider strong and weak electrolytes separately.

Strong electrolytes

Arrhenius argued that, for all electrolytes, the increase in molar conductivity with dilution $\left(\frac{1}{c}\right)$ was due to an increase in the degree of dissociation (α), which reached its maximum value of 1 with infinite dilution. This reasoning of Arrhenius is still acceptable for weak electrolytes, but has not been found adequate for strong electrolytes. This is because the Arrhenius theory does

not consider the strong interionic attractive forces and the ionic mobilities.

According to the Debye-Huckel theory, strong electrolytes are completely dissociated at all concentrations, and the variation of $\wedge m$ with concentration is reasoned on the assumption that every ion is surrounded by an atmosphere of oppositely charged ions. This has the effect of retarding the movement of ions through the solution, hence, reducing the molar conductivity. The increase in molar conductivity with decreasing concentration (or increasing dilution) is thus could be because of lessening of the effects of strong interionic attractive forces. As a result, each ion loses its cloud of oppositely charged ions, becomes free from interionic effects (becomes independent of each other), and reaches its maximum velocity (Figs. 5.4, 5.5). By extrapolation, $\wedge_m$ in very dilute solution can be obtained. This value is known as the molar conductivity at infinite dilution ($\wedge_m^{\infty}$ or $\overset{\circ}{\wedge}_m$). Kohlraush showed that at low concentration, the molar conductivity of strong electrolytes is found to obey the following equation.

$$\wedge_m = \wedge_m^{\infty} - b\sqrt{c} \qquad \text{...(5.10)}$$

Thus, the linear plot of $\wedge_m$ against $\sqrt{c}$ (Fig. 5.5) can be represented by the equation (5·10). In equation (5·10), b is a constant. At infinite dilution, c tends to be zero.

That is, $\wedge_m = \wedge_m^{\infty}$

Weak electrolytes

As stated earlier, Arrhenius theory is able to explain the variation of molar conductivity for weak electrolytes with dilution. This is because they produce so few ions in solution that they are virtually free from the interionic effects discussed earlier. Consequently, $\wedge_m$ appears to be independent on the degree of dissociation (α) of solute. Arrhenius suggested that the fraction α of the solute which is ionized gradually increases with dilution. A α increases with dilution $\left(\frac{1}{c}\right)$ so does $\wedge_m$. The variation of α and hence $\wedge_m$ with $\frac{1}{c}$ or $\sqrt{c}$ is not linear (Figs. 5·4 and 5·5) because of the α^2 term in Ostwald's dilution law, *i.e.*,

$$\frac{1}{c} \propto \frac{\alpha^2}{1-\alpha}$$

or

$$\sqrt{c} \propto \sqrt{\frac{1-\alpha}{\alpha^2}} \qquad \text{...(5.11)}$$

At infinite dilution, α approaches a value of 1 and Λ_m reaches its maximum value Λ_m^∞. The value of degree of ionization at any concentration (c) can be calculated from the measured molar conductivity at that concentration (Λ^c_m). Since

$$\Lambda_m^c \propto \alpha_c$$

$$\Lambda_m^c = k\,\alpha_c$$

where k is constant, α_c is the degree of dissociation at any concentration.

Because $\alpha_c = 1$ at infinite dilution,

$$\Lambda_m^\infty = k$$

Therefore, $$\alpha_c = \frac{\Lambda_m^c}{\Lambda_m^\infty} \qquad ...(5.12)$$

Now it can be concluded that for strong electrolytes, the graph of Λ_m against $\sqrt{c}$ is a straight line, which can be extrapolated to cut the Λ_m axis at Λ_m^∞. From the shape of the graph for a weak electrolyte (Fig. 5·5) it appears that Λ_m^∞ cannot be calculated by extrapolation. Kohlrausch's law enables us to find Λ_m^∞ for weak electrolytes.

Kohlrausch's Law

The molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the ions produced by that electrolyte.

Kohlrausch's finding is based upon the fact for pairs of strong electrolytes than have ions in common, the values of Λ_m^∞ showed an almost constant difference (Table 5.4). The molar conductivity of the cations is denoted by Λ_+^∞ and that of anions Λ_-^∞ then the Kohlrausch's law of independent mobilities of ions is :

$$\Lambda_m^\infty = \nu_+ \Lambda_+^\infty + \nu_- \Lambda_-^\infty \qquad ...(5.13)$$

where ν_+ and ν_- are the number of cations and anions per formula unit of the electrolyte (*e.g.*, $\nu_+ = \nu_- = 1$ for HCl, but $\nu_+ = 1$ and $\nu_- = 2$ for $CaCl_2$).

TABLE 5.4. Molar conductivities at infinite dilution of aqueous electrolytes at 298 K

Electrolyte	Λ_m^{∞} (S m² mol⁻¹)	*Difference* (S m² mol⁻¹)
NaCl	126.5×10^{-4}	Λ_m^{∞} (KCl) $-\Lambda_m^{\infty}$ (NaCl)$=23.4\times10^{-4}$
KCl	149.9×10^{-4}	Λ_m^{∞} (KI)$-\Lambda_m^{\infty}$ (NaI)$=23.5\times10^{-4}$
NaI	126.9×10^{-4}	Λ_m^{∞} (KI)$-\Lambda_m^{\infty}$ (KCl)$=0.5\times10^{-4}$
KI	150.4×10^{-4}	Λ_m^{∞} (NaI)$-\Lambda_m^{\infty}$ (NaCl)$=0.4\times10^{-4}$

Thus, for KCl and NaCl at 298 K,

$$\Lambda_m^{\infty}(\text{KCl})-\Lambda_m^{\infty}(\text{NaCl})=[\Lambda_m^{\infty}(\text{K}^+)+\Lambda_m^{\infty}(\text{Cl}^-)]$$

$$-[\Lambda_m^{\infty}(\text{Na}^+)-\Lambda_m^{\infty}(\text{Cl}^-)]$$

$$=\Lambda_m^{\infty}(\text{K}^+)-\Lambda_m^{\infty}(\text{Na}^+)$$

$$=23{\cdot}4\times10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

Similarly, for KI and NaI

$$\Lambda_m^{\infty}(\text{KI})-\Lambda_m^{\infty}(\text{NaI})=[\Lambda_m^{\infty}(\text{K}^+)+\Lambda_m^{\infty}(\text{I}^-)]$$

$$-[\Lambda_m^{\infty}\,\text{Na}^++\Lambda_m^{\infty}(\text{I}^-)]$$

$$=[\Lambda_m^{\infty}(\text{I}^-)-\Lambda^{\infty}(\text{Cl}^-)]$$

$$=0.5\times10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

For the calculation of α for a weak electrolyte the value of Λ_m^{∞} is required. This cannot be reliably obtained by extrapolation (Fig. 5·5) as it can for strong electrolytes. For example, to calculate Λ_m^{∞} value of acetic acid on the basis of the sum of molar conductivities of H^+ and CH_3COO^- at infinite dilution,

$$\Lambda_m^{\infty}(\text{CH}_3\text{COOH})=\Lambda_m^{\infty}(\text{H}^+)+\Lambda_m^{\infty}(\text{CH}_3\text{COO}^-)$$

we use the following data for strong electrolytes :

Electrolyte	HCl	CH_3COONa	NaCl
Λ_m^{∞} (S m² mol⁻¹)	426.2×10^{-4}	91.0×10^{-4}	126.5×10^{-4}

$$\Lambda_m^{\infty}(CH_3COOH)=\Lambda_m^{\infty}(H^+)+\Lambda_m^{\infty}(CH_3COO^-)$$

$$=[\Lambda_m^{\infty}(H^+)+\Lambda_m^{\infty}Cl^-]$$

$$+[\Lambda_m^{\infty}(Na^+)+\Lambda_m^{\infty}CH_3COO^-]$$

$$-[\Lambda_m^{\infty}(Na^+)+\Lambda_m^{\infty}(Cl^-)]$$

$$=\Lambda_m^{\infty}(HCl)+\Lambda_m^{\infty}(CH_3COONa]-\Lambda_m^{\infty}(NaCl)$$
$$=[426.2\times10^{-4})+(91{\cdot}0\times10^{-4})]-[126.5\times10^{-4}]$$
$$=390.7\times10^{-4}\ S\ cm^2\ mol^{-1}$$

Exercise 5.4. *The molar conductivities of KCl, NaCl and KNO_3 are 150, 126 and 109* S cm² mol⁻¹ *respectively. What is the molar conductivity of $NaNO_3$?*

Solution :

$$\Lambda_m^{\infty}(NaNO_3)=\Lambda_m^{\infty}(NaCl)+\Lambda_m^{\infty}(KNO_3)-\Lambda_m^{\infty}KCl$$

$$=126+109-150$$
$$=85\ S\ cm^2\ mol^{-1}$$

Exercise 5.5. *Find the degree of ionization of acetic acid if an 0·01* M *solution has a molar conductivity (Λ_m^c) of 16.2×10^{-4}* S m² mol⁻¹ *and the value of Λ_m^c is $390{\cdot}7\times10^{-4}$* S m² mol⁻¹.

Solution :

$$\alpha=\frac{\Lambda_m^c}{\Lambda_m^{\infty}}$$

$$=\frac{16{\cdot}2\times10^{-4}}{390{\cdot}7\times10^{-4}}=0{\cdot}042=4{\cdot}2\%$$

5·3 ELECTROLYTIC CELLS

Electrolytic cells are electrochemical cells in which non-spontaneous chemical reactions are made to occur by the forced imput of electrical energy. This process is called electrolysis.

Solutions containing ions conduct electricity whenever a potential difference is applied across electrodes in the solution. Negatively charged ions move towards the anode and positively charged ions to the cathode. The combination of chemical changes occurring at the electrodes is called electrolysis.

Consider the reaction,

Anode	$H_2(g) \longrightarrow 2H^+ + 2e^-$
Cathode	$2e^- + Cl_2(g) \longrightarrow 2Cl^-$
Cell	$H_2(g) + Cl_2(g) \longrightarrow 2H^- + Cl^-$

This reaction is spontaneous but can be reversed by applying an external voltage. This cause the reduction of H^+ to form H_2 and the oxidation of Cl^- to form Cl_2. The reactions are

Cathode :	$2e^- + 2H^+ \longrightarrow H_2(g)$
Anode :	$2Cl^- \longrightarrow Cl_2(g) + 2e^-$
Cell	$2H^+ + Cl^- \longrightarrow H_2(g) + Cl_2(g)$

This is an example of electrolysis, a process in which an otherwise non-spontaneous reaction is forced to take place by the application of energy from an external source. Reaction at the anode always involves electron loss and thus is termed anodic oxidation, while that at the cathode requires electrons and is known as cathodic reduction. Electrons are released at the anode and consumed at the cathode, and therefore, they travel through the external circuit from anode to cathode. Since the reaction is non-spontaneous, the external source of electrical energy forces electrons to flow from the positive electrode to the negative electrode. Thus the anode is the positive electrode and the cathode the negative electrode in all electrolytic cells. Figure 5.6 shows an electrolytic cell.

Consider the electrolysis of a solution of sodium chloride in water. Because there are so many species present in the cell, several possibilities exist for both anode and cathode reactions. Possible anode (oxidation) reactions :

$$2Cl^- \longrightarrow Cl_2(g) + 2e^-$$
$$2H_2O \longrightarrow O_2(g) + 4H^+ + 4e^-$$
$$4OH^- \longrightarrow O_2(g) + 2H_2O + 4e^-$$

Possible cathode (reduction) reactions :

$$e^- + Na^+ \longrightarrow Na(s)$$
$$2e^- + 2H_2O \longrightarrow H_2(g) + 2OH^-$$
$$2e^- + 2H^+ \longrightarrow H_2(g)$$

The half-reactions and overall cell reaction for electrolysis of aqueous sodium chloride solution are :

$$2Cl^- \longrightarrow Cl_2+2e^- \qquad \text{(At anode)}$$
$$2H_2O+2e^- \longrightarrow 2OH^-+H_2 \qquad \text{(At cathode)}$$
$$\underbrace{2H_2O+2Cl^-}_{\underbrace{+2Na^+}_{2\,NaCl}} \longrightarrow \underbrace{2OH^-}_{\underbrace{2Na^+}_{2\,NaOH}}+H_2+Cl_2 \quad \text{(Overall cell reaction)}$$

As discussed earlier, the electrons flow from the anode (+) through the external circuit to the cathode (−) under the influence of electrical energy that causes the non-spontaneous cell reaction to occur.

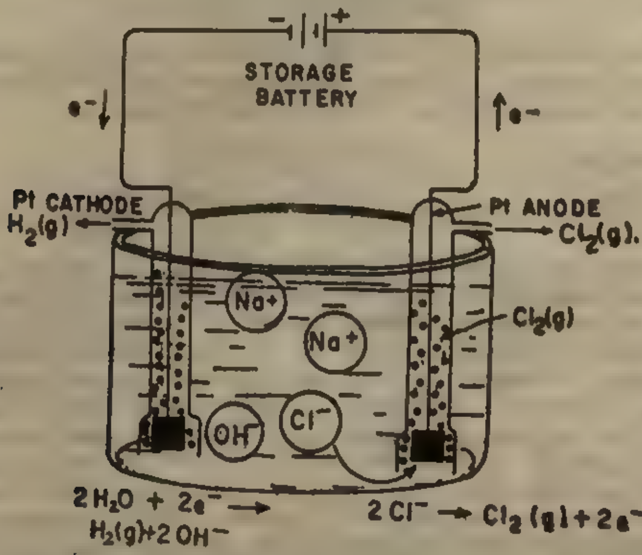


Fig. 5.6. Electrolysis of aqueous NaCl solution.

Although several reactions occur at both the anode and cathode, the net result is the production of H_2(g) and NaOH (aq) at the cathode and Cl_2 (g) at the anode.

5.3.1. Faraday's Laws

In 1832, Michael Faraday developed the quantitative statements now known as Faraday's Laws of Electrolysis. These are (1) that the amount of a substance produced by electrolysis at each electrode is directly proportional to the quantity of electricity that passes through the cell, and (2) that for a given quantity of electricity the amount of a substance produced is proportional to its equivalent mass.

To illustrate the Faraday's first law, consider the electrolysis of molten NaCl. At the cathode the half-reaction is,

$$Na^+ + e^- \longrightarrow Na\ (s) \qquad \text{(At cathode)}$$

The above equation shows that one electron is required to produce one sodium atom. This means that one mole of electrons are required to produce one mole of sodium atoms.

As we know, the charge on one electron to be 1.601×10^{-19}C, the charge on one mol (6.023×10^{23}) of electrons is (6.023×10^{23}) electrons mol^{-1} $\times$ (1.601×10^{-19}C) electron^{-1} = 96488 C mol^{-1}.

The charge of 1 mol of electrons (96488 C mol^{-1}) is called one faraday (1 F) in honour of Michael Faraday who discovered quantitative laws governing electrolysis.

$$F = 96488 \text{ C mol}^{-1} \text{ or approximately } 96500 \text{ C mol}^{-1}$$

Further, if one coulomb of electricity passes through a conductor in one second, we say that the conductor carries an electrical current of one ampere (A). In other words, one ampere equals one coulomb per second.

An illustration of Faraday's second law can also be found in the electrolysis of molten NaCl. At the anode the half-reaction is,

$$2\,Cl^- \longrightarrow Cl_2\,(g) + 2e^- \qquad \text{(At anode)}$$

In this reaction, two electrons have been withdrawn (from two Cl^- ions) in order to produce one Cl_2 molecule. That is, two moles of electrons are required to produce one mole of Cl_2 molecules. This means that one mole of electrons will produce 0.5 mol of Cl_2 molecules. Thus one faraday of electricity will produce one equivalent (1 mol) of Na at the cathode and one equivalent (0.5 mol) of Cl_2 at the cathode. Now we can have the expression.

$$Q = n\,F$$

Here Q is the charge and n is the number of mole of electrons

Exercise 5.6. *Calculate the mass of copper metal and of oxygen gas produced by the electrolysis if $CuSO_4$ solution on passing 5.0 ampere of current through a solution of copper (II) sulphate for 1.5* hr. *What would be the volume of oxygen at STP ?*

Solution. The equation for the reduction of Cu(II) ions is

Cu^{2+} +	$2e^-$ $\longrightarrow$	Cu	(At cathode)
1 mol	$2\,(6.02 \times 10^{-3})e^-$	1 mol	
63.5 g	2 (96500 C)	63.5 g	

Since the electrode half-reactions can be interpreted in terms of faradays of electricity, we will first calculate the number of faradays passing through the cell. Since one ampere is one coulomb per second, the total number of coulombs flowing through the cell is

$$\frac{5.0\text{ C}}{s} \times 1.5\text{ hr} \times \frac{60\text{ min}}{1\text{ hr}} \times \frac{60\text{ s}}{1\text{ min}} = 2.7 \times 10^4\text{ C}$$

$$= 0.28\text{ F}$$

$$(1\text{ F} = 96500\text{ C})$$

From the reduction equation it is evident that one mol of copper is produced from two faradays of electricity, and so the amount of copper produced is

$$0.28\ F \times \frac{1\ \text{mol of Cu}}{2\ F} \times \frac{63.5\ \text{g Cu}}{1\ \text{mol of Cu}} = 8.9\ \text{g of Cu}$$

Now consider the reaction taking place at anode,

$$2H_2O \longrightarrow O_2(g) + 4H^+ + 4e^-$$

From the reaction it is evident that one mol of O_2 is produced from 4 faradays of electricity, and so the amount of O_2 produced is,

$$0.28\ F \times \frac{1\ \text{mol of } O_2}{4\ F} \times \frac{32\ \text{g of } O_2}{1\ \text{mol of } O_2} = 2.2\ \text{g of } O_2$$

For every 4 F of electricity 22.4 litres of O_2 at STP are produced, therefore, the volume of oxygen produced at STP is

$$= 0.28\ F \times \frac{22.4\ L}{4\ F} = 1.568\ L.$$

Exercise 5.7. *150* mL *of hydrogen was produced and collected over water at a total pressure of 752* mm Hg *and 301* K *on passing current through the acidulated water for 1* hr. *Calculate the average current which was passed during electrolysis (The vapour pressure of H_2O at 301* K *is 28* mm Hg).

Solution. To find the number of mol of H_2 gas we use the ideal gas law. The partial pressure of H_2 is 752−28=724 mm Hg.

$$n = \frac{PV}{RT} = \frac{724\ \text{mm Hg}\left(\frac{1\ \text{atm}}{760\ \text{mm Hg}}\right)0.15L}{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ 301K}$$

$$= 5.7 \times 10^{-3}\ \text{mol}$$

The reduction half reaction is,

$$2e^- + 2H^+ \longrightarrow H_2(g) \qquad \text{(At cathode)}$$

Since, two faradays of electricity are required to produce one mol of H_2, the number of faradays of electricity passed is,

$$5.7 \times 10^{-3} \times \frac{2F}{1\ \text{mol of } H_2} = 1.14 \times 10^{-2} F$$

$$= 1100\ C$$

Since 1100 C of electricity passes through water for 1 hr, the average number of coulombs per second is,

$$\frac{1100\ C}{60 \times 60\ s} = 0.306\ C\ s^{-1}$$

5.4. VOLTAIC OR GALVANIC CELLS

Voltaic or galvanic cells are electrochermical cells in which spontaneous oxidation-reduction reactions produce electrical energy. The two halves of the redox reaction are separated, so that the electrons produced at one electrode are forced to travel through

an external circuit to the other electrode. This is how useful electrical energy is obtained.

A metal strip dipping in a solution is known as a half-cell or an electrode. The reaction that takes place in a half-cell is known as half-cell reaction. When two half-cells are connected internally by a porous diaphragm or a salt bridge and externally by a conductor, this assembly will constitute an electrochemical or galvanic or voltaic cell (Fig. 5.7).

The zinc copper cell

A voltaic cell in which one electrode is zinc placed in zinc sulphate solution and the other is, copper in copper sulphate solution is called **Daniell cell** (Fig. 5.7). Many voltaic cells can be set up on the lines of zinc-copper cell. A cell in which the reactants and products are in their thermodynamic standard states (one molar concentration for dissolved ions and one atmosphere partial pressure for gases) is called a **standard cell.**

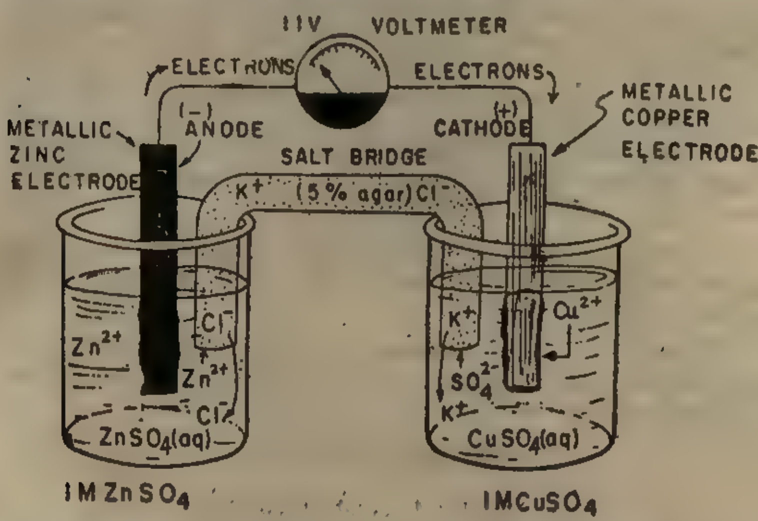


Fig. 5.7. An assembly showing an electrochemical change. A difference in potential is established between the two metal electrodes. Electrical contact between the solutions is established through a salt bridge that allows the migration of ions but not that of solutions. Electrons migrate through the wire connecting the electrodes externally. Thus a complete circle is established.

The following observations are made in the zinc-copper cell as the cell operates :

(*i*) The voltmeter reads the voltage 1.1 between the two electrodes.

(*ii*) The mass of copper electrode increases, and the concentration of Cu^{2+} decreases in the solution around copper electrode.

(*iii*) The mass of zinc electrode decreases, and the concentration of Zn^{2+} ions increases in the solution around the zinc electrode.

These observations suggest that oxidation takes place at the zinc electrode (anode) and the reduction takes place at the copper electrode (cathode). Here, copper ions are reduced and the resulting copper atoms deposit on the surface of the copper electrode in a process called **plating out**.

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad \text{(anode half-reaction)}$$
$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \text{(cathode half-reaction)}$$
$$Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+} \qquad \text{(overall cell-reaction)}$$

As the cell operates, electrons are released at the anode and consumed at the cathode, *i.e.*, electrons travel the external circuit from the anode to the cathode. Since the electrons flow spontaneously in all voltaic cells, they migrate from the negative electrode to the positive electrode. So, in contrast to the electrolytice cells, the anode here is negative and the cathode is positive. In order to maintain electroneutrality and complete the circuit the two halves of the cell are joined by a salt bridge.

The flow of electrons depends upon the tendencies for anode and cathode half-reactions to occur. The voltmeter measures the tendency of electrons to flow.

Galvanic cells are commonly represented in a shorthand notation called a cell diagram. The cell diagram for the Daniell cell is illustrated below :

Electrode surfaces

$Zn \mid Zn^{2+}(1.0M) \parallel Cu^{2+}(1.0M) \mid Cu$

(LHS) Anode (−) Cathode (+) (RHS)

Salt-bridge

Species (and concentrations)
in contact with electrode surfaces

Here, each symbol and formula has its usual meaning, and the short vertical lines represent phase boundaries or junctions. Conventionally, the anode is written on the left-hand side (LHS) and the cathode is written on the right hand side (RHS). A salt bridge or porous partition to minimize the liquid junction potential is indicated by a double vertical line.

Salt bridge and its functions

The saturated solution of salt (*e.g.*, KCl, KNO_3 or NH_4NO_3) mixed with gelatin or agar gel is filled in a glass tube (bent according to requirement) which connects the two electrolytes like a bridge, hence, the name salt bridge. This does not permit bulk flow of solution between compartments (two halves of the cell) but allows the migcation of ions to establish an electrical continuity within the cell. It also reduces the so-called liquid-junction potential, a voltage produced where two dissimilar solutions are in contact. This voltage arises because of unequal rates of anion and cation migration across the contact region or junction. The ions present in the salt bridge migrate at equal rates.

In the presence of salt bridge (Fig. 5.7), the negative ions move from the cathode compartment through salt bridge to anode compartment. The positive ions move in the reverse direction. Thus, the salt provides cations and anions to replace the ions lost or produced at the two electrodes. For example, in the anode compartment, additional Zn^{2+} ions appear which are balanced by Cl^- ions supplied by salt bridge. Similarly, in the cathode compartment additional SO_4^{2-} ions appear due to the reduction of Cu^{2+} ions. SO_4^{2-} ions are balanced by K^+ ions supplied by salt bridge.

Porous partion and its functions

Sometimes a porous partion is used (Fig. 5.8) to separate the two halves of the cell. This is less efficient but a more practical

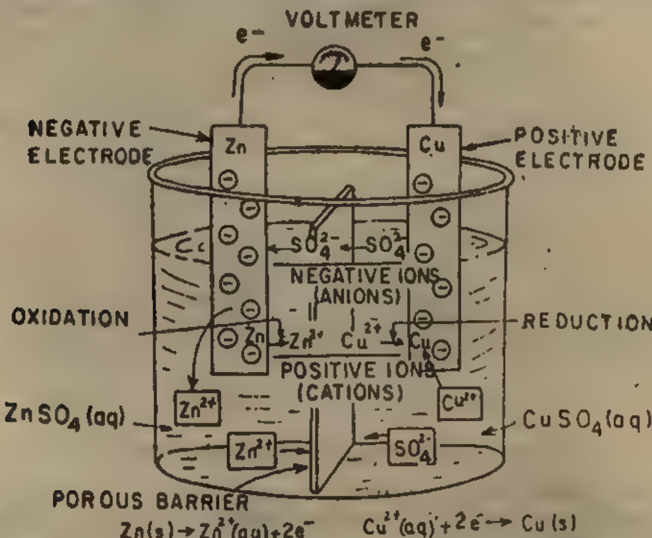


Fig. 5.8. A diagrammatic view of a zinc-copper electrochemical cell with a porous diaphragm or partition to prevent the mixing of two electrolytes contained in the cell.

method. It is employed in the commercial form of Daniell cell (discussed later under commercial cells). The partion allows the migration of ions when the cell operates. It decreases the diffusion of ions to a significant extent when the cell is not in use.

The copper-silver cell

Let us now consider another standard voltaic cell (Fig. 5.9) consisting of a strip of copper immersed in 1.0 m copper (II) sulphate solution and a strip of silver immersed in 1.0 M silver nitrate solution. The figure suggests that the copper strip behaves as anode in this cell because copper metal is oxidized to Cu^{2+} ions. The silver strip behaves as cathode because reduction of Ag^+ ions take place on it.

$$Cu \longrightarrow Cu^{2+} + 2e^- \quad \text{(anode half-reaction)}$$

$$(Ag^+ + e^- \longrightarrow Ag) \times 2 \quad \text{(cathode half-reaction)}$$

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag \quad \text{(overall cell-reaction)}$$

In the zinc-copper cell, the copper electrode is the cathode, while in the copper-silver cell the copper electrode is the anode.

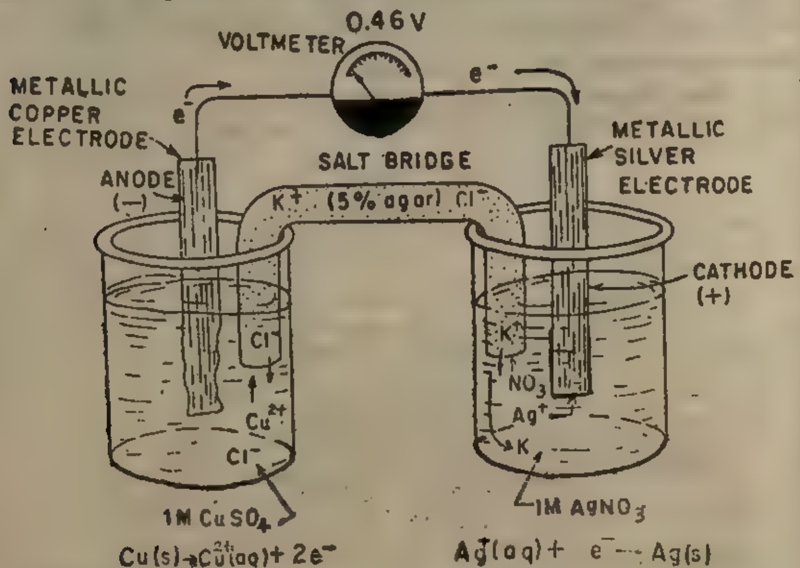


Fig. 5.9. The copper-silver voltaic cell.

The behaviour of an electrode as an anode or a cathode depends on its coupling with the other electrode of the cell. In the cell (Fig. 5 7) described earlier, Cu^{2+} ion is a stronger oxidizing agent than Zn^{2+} ion and Cu^{2+} ion oxidizes metallic zinc to Zn^{2+} ion. By contrast, in the cell (Fig. 5·9) given here, Ag^+ ion is a stronger oxidizing agent than Cu^{2+} ion, and Ag^+ oxidizes copper metal to Cu^{2+}. In other words, metallic zinc has a stronger tendency to under-

go oxidation than metallic copper and metallic copper has a stronger tendency to undergo oxidation than metallic silver., *i.e.*,

Oxidizing agents	**Reducing agents**
$Zn^{2+} < Cu^{2+} < Ag^{+}$	$Ag < Cu < Zn$
$\longrightarrow$	$\longrightarrow$
Increasing strength	Increasing strength

5.5. ELECTRODE POTENTIAL AND ELECTROMOTIVE FORCE

The oxidizing power or reducing power of an element or a compound can be determined experimentally by means of a galvanic cell. In such a cell, the reaction takes place spontaneously because one atom or ion attracts electrons more strongly than the other. The electron attracting power of an electrode is called its potential. Alternatively, the tendency to lose electrons by conductors is called **electrode potential.**

There are three possibilities when a metal plate (M) is immersed in a solution containing the ion M^{n+} (Fig. 5.10).

(*i*) A metal ion M^{n+} may come in the contact of the electrode and experience no change.

(*ii*) A metal ion M^{n+} may come in the contact of the electrode, accept *n* electrons and be reduced to a metal atom M.

$$M^{n+} + ne^- \longrightarrow M$$

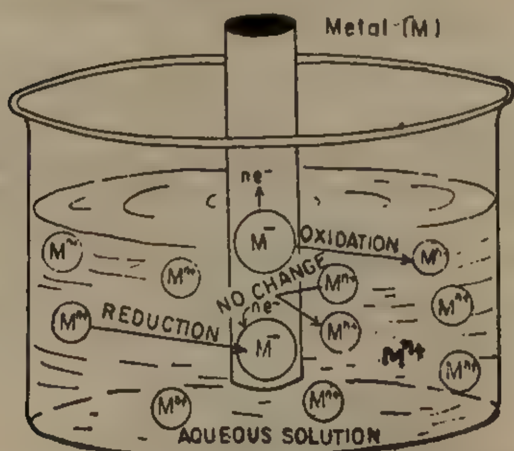


Fig. 5.10. Electrode equilibrium

$$M(s) \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^-$$

(*iii*) A metal atom on the electrode M may oxidize and thereby lose n electrons to the electrode and enter the solution as M^{n+}.

$$M(s) \longrightarrow M^{n+} + ne^-$$

When dynamic equilibrium is attained, a small difference in electrical potential exists between the metal electrode and the solution. A metal with a strong tendency of losing electrons, imparts M^{n+} ions to solution resulting in a fractional increase in the number of metal ions, M^{n+} in solution and a fractional increase in the number of electrons on the electrode. As a result, the electrode develops a small negative potential with respect to the solution. Alternatively, metal ions may take electrons from the strip of metal and be discharged as metal atoms. In this case, the metal will become positively charged.

In combination with a second metal strip in solution, however, a mutual exchange of electrons can take place, giving rise to a redox reaction. The forward oxidation reaction or backward reduction reaction of an electrode depends on the nature of the second electrode with which it is combined.

The potential difference between the strip of a metal and the solution depends upon the nature of metal and on the concentration of the ions involved in the equilibrium at the metal surface. Zinc acquires a more negative potential than copper, since it has a greater tendency to dissolve as ions and a smaller tendency to be deposited as metal.

Thus, in the Daniell cell, zinc has a greater tendency for oxidation than copper. Conversely, Cu^{2+} ions have a greater tendency for reduction than Zn^{2+} ions. The potential difference across the two electrodes is called **electromotive force** (abbreviated as *emf* or EMF). It measures the tendency of electrons to flow through the external circuit.

5.5.1. Standard Electrode Potential

The tendency for a metal to get oxidized or conversion of its ions into metal by reduction is measured by the equilibrium constant, K

$$Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^-$$

$$\text{Therefore,} \quad K = \frac{[Cu^{2+}(aq)]\,[e^-]^2}{[Cu(s)]}$$

or $\quad [Cu^{2+}(aq)] = K[Cu(s)] = K$ (Since $\quad [Cu(s)] = 1$ and $[e^-]^2 = 1$

This tendency can also be expressed in terms of potential developed between the metal and its ions.

The potential difference at equilibrium depends on :

1. the metal and its ions,
2. the concentration of the ions in the solution, and
3. temperature.

The potential difference between an electrode and the metal ions at 1 molar concentration (or at unit activity) and at 298K is called standard electrode potential ($E°$). The definition of standard electrode potential can thus be, $Cu^{2+}(aq)$ (1 mol L^{-1})$+2e^- \rightarrow$ Cu(s).

This is usually expressed as reduction reaction, hence, it is called **standard reduction potential**. By convention, standard electrode potential is taken for a half-cell described by a reduction reaction.

The potential of a single electrode cannot be measured because when the second metal is dipped in the electrolyte to make the measurement, the metal becomes another electrode. Thus, we select *one* electrode arbitrarily as a standard and measure the **potential difference** between this standard electrode and any other electrode. By general convention (IUPAC recommendation), **standard hydrogen electrode** (abbreviated as SHE) is taken as the standard referenae electrode. Its standard electrode potential has been assumed to be zero volt. It is pictured in Fig. 5.11.

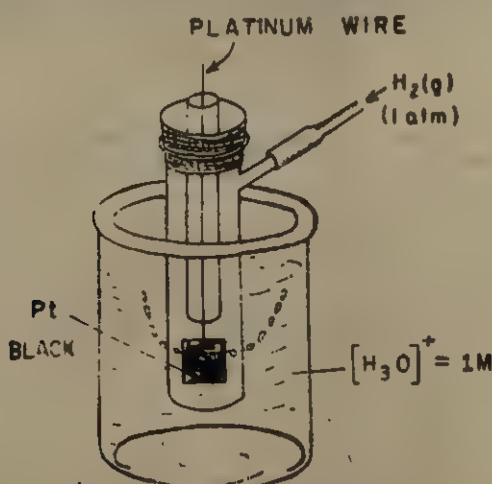


Fig. 5.11. Hydrogen electrode.

A pure metal dipped in one molar solution of one of its ions (or in case a gas is involved, it is at a partial pressure of one atmosphere), is referred to as the **standard electrode**. When such an electrode is coupled with SHE, the measured potential is called

the **standard electrode potential**. The symbol E is used to denote cell and electrode potentials ; and $E°$ for standard electrode potentials.

Hydrogen electrode

It consists of platinum electrode coated with platinum black, immersed in a 1M $[H_3^+O]$ solution saturated with H_2 gas at 1 atm at 298K. Platinum black catalyzes the attainment of equilibrium between the H_2 gas and H^+ ions in the solution (Fig. 5.11).

$$H_2(g)+H_2O(l) \rightleftharpoons 2H_3O^+(aq)+2\,e^-$$

A potential develops on the surface of platinum. Pure hydrogen (1 atm) is constantly bubbled around a platinum electrode immersed in an acid solution of unit activity. (IM HCl). It can be represented as Pt $H_2(g)$ (1 atm) ; H_3O^+ (a=1).

The need for specifying the hydrogen gas pressure and the exact concentration of H^+ in solution arises because the equilibrium value of electrode potential (in combination with hydrogen electrode) depends on these variables. The increase in hydrogen ion $[H_3O]^+$ concentration favours the forward reaction and the increase in $H_2(g)$ pressure favours the backward reaction.

The only practical difficulty in setting this electrode is the maintenance of 1 atm gas pressure. Several secondary electrodes, whose potentials are known on the hydrogen scale, are used in place of hydrogen electrode.

Calomel electrode

It is a secondary reference electrode (Fig. 5.12). This consists of mercury, solid mercury (I) chloride and a solution of potassium chloride (0.1 M or 1 M or saturated solution of KCl). The electrode is represented as Hg, $Hg_2Cl_2(s)$; KCl(aq).

Mercury of a high degree of purity is used. Calomel electrode consists of glass tube ; mercury is placed at the bottom of it. Mercury is covered with a paste of mercurous chloride. A saturated solution of KCl is filled in the tube above the paste. A platinum wire is fused in a glass tube to make electrical contact.

The half-cell reaction is :

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2\,Hg(l) + 2\,Cl^-(aq)$$

The potentials of the calomel electrode determined using standard hydrogen electrode for different concentrations of potassium chloride at 298 K are given below :

For 0.1 M KCl solution	$E=-0{\cdot}3338$ V
For 1 M KCl solution	$E=-0{\cdot}2800$ V
For saturated KCl solution	$E=-0{\cdot}2415$ V

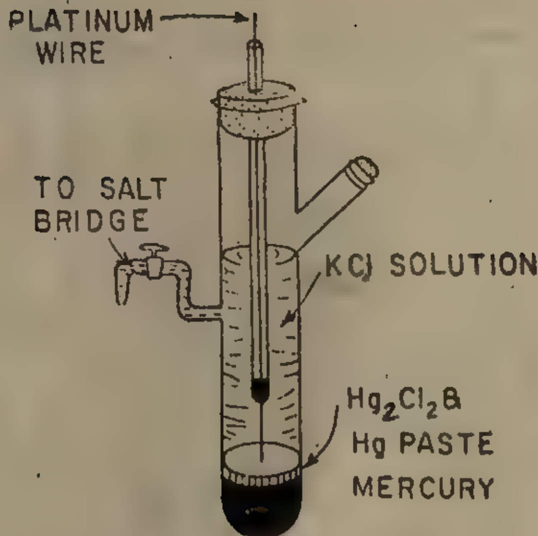


Fig. 5.12. Calomel electrode.

5.5.2. Determination of Standard Electrode Potential

The oxidation-reduction potential of an electrode can be measured by coupling it with the standard hydrogen electrode. A potential difference is developed between the two electrodes due to the movement of electrons from the point of supply to the point of demand. This difference can be measured if the flow of electrods can be channelled and made to pass through voltmeter The overall potential difference represents the difference between the oxidation potential for the electrode which undergoes oxidation and the electrode which undergoes reduction.

For example, zinc electrode when combined with SHE is oxidized to Zn^{2+} ions. In other words, the zinc electrode pushes electrons into the external circuit and forms the anode. By convention, the anode is shown on the left (Fig. 5.13) and it is said to possess a negative value of **reduction electrode potential.**

As the cell operates, the mass of the zinc electrode decreases and the concentration of Zn^{2+} ions increases in the solution around the electrode. The $[H_3^+O]$ ion concentration decreases in SHE, and hydrogen gas is produced.

At anode	$Zn(s) \rightarrow Zn^{2+}(aq)+2e^-$	$E^\circ = 0.76\ V$
At cathode	$2H_3^+O(aq)+2e^- \rightarrow H_2(g)+2H_2O(l)$	$E^\circ = 0.00\ V$
Cell reaction	$Zn(s)+2H_3^+O(aq) \rightarrow Zn^{2+}(aq)+2H_2O$	$E^\circ_{cell} = 0{\cdot}76\ V$

Since the cell potential is found to be 0.76 V and the potential of SHE is 0.00 V, the standard oxidation potential of the zinc electrode (anode) is 0·76 V and the standard reduction potential is −0·76 V.

The cell notation is,

$$Zn\ ;\ Zn^{2+}\ (1M)\ \|\ H_3^+O\ (1M)\ ;\ H_2\ (1\ atm),\ Pt$$

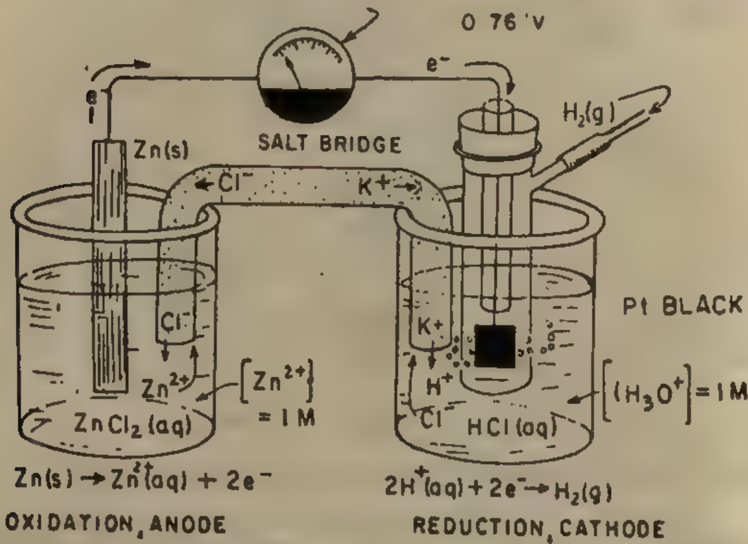


Fig. 5.13. A half cell Zn^{2+}/Zn in combination with SHE. Zinc electrode acts as anode and SHE acts as cathode. The $E°_{Zn^{2+}/Zn}$ is —0·76 V.

A positive emf of the cell indicates that the cell reaction proceeds spontaneously.

By definition, the emf of a cell is given by

$$E_{cell} = E_{RHC} = E_{LHC} \qquad ...(5{\cdot}14)$$

where E_{RHC} and E_{LHC} are the reduction potentials of the right-hand and left-hand cells respectively. As the emf of the cell under reference is +ve, it means E_{RHC} is greater them E_{LHC}. This implies that the reduction tendency of H^+ ion appearing on the right-hand cell is greater than Zn^{2+} appearing on the left-hand cell.

The negative sign of the standard reduction potential of zinc electrode indicates that the half cell reaction actually takes place in the opposite direction, that is, as an oxidation rather than as a reduction half-reaction. It also implies that electrons tend to emerge from zinc electrode and hence the electrode is the anode. The zinc electrode is thus negative with respect to the hydrogen electrode.

Now consider a cell in which the standard hydrogen electrode is coupled with a standard copper electrode (Fig. 5.14).

$$Cu \mid Cu^{2+}\,(1{\cdot}0\ M) \parallel H_3^+O\,(1.0\ M)\ H_2(g)\,(1{\cdot}0\ atm) \mid Pt$$

As the cell operates, the mass of the copper electrode increases and the concentration of Cu^{2+} ions decreases in the solution around the copper electrode. The H$^+$ concentration increases in the solution as a result of use and oxidation of hydrogen gas.

At anode	$H_2(g)+H_2O(l) \rightarrow 2H_3^+O+2e^-$	$E°=0{\cdot}00\ V$
At cathode	$Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$	$E°=0{\cdot}343\ V$
Cell reaction	$H_2(g)+Cu^{2+}(aq) \rightarrow 2H_3^+O+Cu(s)$	$E°_{cell}=0.34\ V$

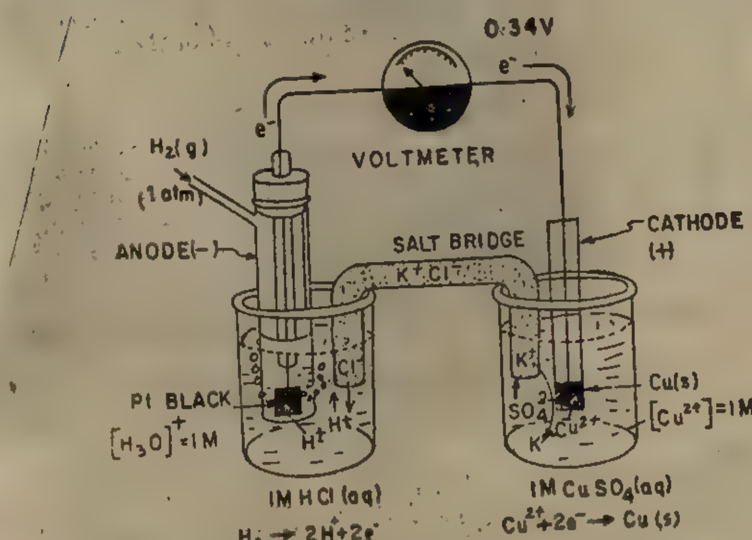


Fig. 5.14. The half cell Cu^{2+}/Cu in combination with SHE. Copper electrode acts as cathode and SHE acts as anode. The $E°_{Cu^{2+}/Cu}$ is 0·34 V.

That is, the standard reduction potential of the copper electrode is 0.34 V. The positive electrode potential of the copper half-cell means that with respect to the standard hydrogen electrode, the half-reaction is reduction as written. The copper electrode is thus cathode where Cu^{2+} ions are reduced to copper metal.

Now we are in a position to conclude that the positive and negative signs of copper and zinc electrode potentials signify the direction in which the reaction occurs spontaneously with respect to the hydrogen half-cell. If a half-reaction occurs or is written in the opposite direction, we must reverse the sign of the potential.

Thus, if we have a cell in which the left-hand cell is the standard hydrogen half-cell and the right-hand half-cell constitutes the half-cell system whose potential, relative to that of the standard hydrogen half-cell is required, then according to equation (5.14) we have

$$E_{RHC}=E_{cell}+0=E_{cell}$$

that is, the reduction potential of the given cell is numerically equal to the emf of the cell.

The sign of the electrode reduction potential is the experimentally measured sign of the cell emf if the SHE is on the left and the electrode under reference is on the right.

Thus, the nature of the electrode of half-cell (whether positive or negative), in a cell in which the other half-cell is the standard hydrogen ion half cell, is determined by the sign of the reduction potential of the given half-cell.

Table 5.5 lists some standard electrode (reduction) potentials at 298 K. This table can be used for (*i*) predicting the voltage which a given standard galvanic cell would produce, (*ii*) predicting the spontaneity of a given redox reaction, (*iii*) comparing the relative strengths of oxidizing agents, and (*iv*) comparing the relative strengths of reducing agents. For predicting cell voltages, it is always necessary to add the potential for an oxidation half-reaction to that for the reduction half-reaction which is coupled with it. Hence, this table is sometimes referred to as an **electrochemical series.**

TABLE 5.5. Some standard electrode (or reduction) potential at 298K in acid solution (electrochemical series)

Electrode (Couple)	*Electrode reaction*	*E° at 298 K (Volt.)*
Li^+/Li	$Li^++e^- \rightarrow Li$	−3.05
M^+/M (M=K, Rb or Cs)	$M^++e^- \rightarrow M$	−2.93
Ba^{2+}/Ba	$Ba^{2+}+2e^- \rightarrow Ba$	−2.90
Sr^{2+}/Sr	$Sr^{2+}+2e^- \rightarrow Sr$	−2.89
Ca^{2+}/Ca	$Ca^{2+}+2e^- \rightarrow Ca$	−2.76
Na^+/Na	$Na^++e^- \rightarrow Na$	−2.71
Mg^{2+}/Mg	$Mg^{2+}+2e^- \rightarrow Mg$	−2.38
Al^{3+}/Al	$Al^{3+}+3e^- \rightarrow Al$	−1.67
H_2O/OH^-	$2H_2O+2e^- \rightarrow H_2+2OH^-$	−0.83
Zn^{2+}/Zn	$Zn^{2+}+2e^- \rightarrow Zn$	−0.76
Cr^{3+}/Cr	$Cr^{3+}+3e^- \rightarrow Cr$	−0.74
Fe^{2+}/Fe	$Fe^{2+}+2e^- \rightarrow Fe$	−0.44
Cd^{2+}/Cd	$Cd^{2+}+2e^- \rightarrow Cd$	−0.40

(Contd.)

(Contd.)

Electrode (Couple)	*Electrode reaction*	*E° 298 K (Volt.)*
$SO_4^{2-}/Pb, PbSO_4$	$PbSO_4+2e^- \rightarrow Pb+SO_4^{2-}$	−0.31
Co^{2+}/Co	$Co^{2+}+2e^- \rightarrow Co$	−0.28
Ni^{2+}/Ni	$Ni^{2+}+2e^- \rightarrow Ni$	−0.25
Sn^{2+}/Sn	$Sn^{2+}+2e^- \rightarrow Sn$	−0.14
Pb^{2+}/Pb	$Pb^{2+}+2e^- \rightarrow Pb$	−0.13
$H^+/\frac{1}{2}H_2, Pt$	$H^+ + e^- \rightarrow \frac{1}{2}H_2$	−0.00 (by definition)
Sn^{4+}/Sn^{2+}	$Sn^{4+}+2e^- \rightarrow Sn^{2+}$	0.15
Cu^{2+}/Cu^+	$Cu^{2+}+e^- \rightarrow Cu^+$	0.15
Cu^{2+}/Cu	$Cu^{2+}+2e^- \rightarrow Cu$	0.34
Cu^+/Cu	$Cu^+ + e^- \rightarrow Cu$	0.52
$\frac{1}{2}I_2/I^-$	$\frac{1}{2}I_2 + e^- \rightarrow I^-$	0.54
Fe^{3+}/Fe^{2+}	$Fe^{3+}+e^- \rightarrow Fe^{2+}$	0.77
Hg_2^{2+}/Hg	$\frac{1}{2}Hg_2^{2+}+e^- \rightarrow Hg$	0.80
Hg^{2+}/Hg	$Hg^{2+}+2e^- \rightarrow Hg$	0.85
NO_3^-/NO	$NO_3^-+4H^++3e^- \rightarrow NO(g)+2H_2O$	0.97
O_2/H_2O	$O_2+4H^++4e^- \rightarrow 2H_2O$	+0.82
$Cr_2O_7^{2-}/Cr^{3+}$	$Cr_2O_7^{2-}+14H^++6e^- \rightarrow 2Cr^{3+}+7H_2O$	1.33
Cl_2/Cl^-	$Cl_2(g)+2e^- \rightarrow 2Cl^-$	1.36
MnO_4^-/Mn^{2+}	$MnO_4^-+8H^++5e^- \rightarrow Mn^{2+}+4H_2O$	1.51
F_2/F^-	$F_2(g)+2e^- \rightarrow 2F^-(aq)$	2.87

Exercise 5·6. *Calculate the voltage produced by a galvanic cell using the standard electrode potentials in Table 5.5.*

$$Mg \mid Mg^{2+} \parallel Cu^{2+} \mid Cu$$

Solution. The half reactions and their voltages are :

$$Mg(s) \rightarrow Mg^{2+}(aq)+2e^- \qquad E^\circ = 2{\cdot}38V$$
$$Cu^{2+}(aq)+2e^- \rightarrow Cu(s) \qquad E^\circ = 0{\cdot}34V$$
$$\text{Cell reaction } Mg(s)+Cu^{2+}(aq) \rightarrow Mg^{2+}(aq)+Cu(s) \qquad E^\circ = 2{\cdot}72V$$

Since the cell potential is positive, the cell reaction

$$Mg(s)+Cu^{2+}(aq) \rightarrow Mg^{2+}(aq)+Cu(s)$$

will occur as written.

Exercise 5.7. *Predict whether or not the following reaction can occur (all Reactants and Products in their standard states).*

$$Sn(s)+Fe^{2+}(aq) \rightarrow Sn^{2+}(aq)+Fe(s)$$

Solution. Adding the oxidation potential to the reduction potential (Table 5.5), we have

$$\text{Oxidation } Sn(s) \rightarrow Sn^{2+}(aq)+2e^- \qquad E^\circ = 0.14V$$
$$\text{Reduction } Fe^{2+}(aq)+2e^- \rightarrow Fe(s) \qquad E^\circ = -0.44V$$
$$\text{Cell reaction } Sn(s)+Fe^{2+}(aq) \rightarrow Sn^{2+}(aq)+Fe(s) \qquad E^\circ = -0.30V$$

The negative cell potential indicates that the cell reaction is non-spontaneous ; it cannot occur. For the cell reaction to occur spontaneously, the actual reaction would be

$$Fe(s)+Sn^{2+}(aq) \rightarrow Fe^{2+}(aq)+Sn(s)$$

5.5.3. Dependence of EMF on Concentration and Temperature.

The half-cell potentials given in Table 5.5 are the standard potentials where the reactants have been in their standard states, i.e. the concentrations of ions and the pressure of gascous substances have been assumed to be in the standard unit concentration (=1 mole dm^{-3} or 1 mol L^{-1}) and standard unit pressure (=101·325 k Pa=1 atm) respectively.

At conditions other than standard conditions, the electrode potential is given by the Nernst equation

$$E=E^{\circ}-\frac{RT}{nF}\ ln\ Q \qquad ...(5.15)$$

In this equation, Q is the standard reaction quotient of the half-cell reaction that has the same form as the expression for the equilibrium constant but the concentrations are not the equilibrium concentrations. In the expression, n is the number of electrons involved in the half-cell reaction, F is the faraday constant (=96500C mol^{-1}), R is the gas constant (8.314 JK^{-1}), T=kelvin temperature and the symbol ln stands for the natural logarithms to the base e.

For a reaction of the type,

$$M^{n+}ne^{-} \rightarrow M$$

$$Q=\frac{1}{[M^{n+}]} \qquad ...(5.16)$$

This is because the molar concentration of M, the solid phase has a constant value and Q includes it. Therefore the expression (5·15) becomes

$$E_{M^{n+}/M}=E^{\circ}_{M^{n+}/M}-\frac{RT}{nF}\ln\frac{1}{[M^{n+}]} \qquad ...(5.17)$$

Since the emf of a complete cell is the algebraic sum of the two halves-cell potentials, it must also depend upon the temperature and concentration (or pressure) of the species involved in the overall cell reaction. For the Daniell cell,

$$Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$$

Negative electrode	Positive electrode
Anode	Cathode
LHC	RHC

from the equation (5.14) we have

$$E_{cell}=E_{RHC}-E_{LHC}$$

$$=\left[E^\circ_{Cu^{2+}/Cu}-\frac{RT}{2F}\ln\frac{1}{[Cu^{2+}]}\right]$$

$$-\left[E^\circ_{Zn^{2+}/Zn}-\frac{RT}{2F}\ln\frac{1}{[Zn^{2+}]}\right]$$

$$=\left(E^\circ_{Cu^{2+}/Cu}-E^\circ_{Zn^{2+}/Zn}\right)-\frac{RT}{2F}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

or
$$E_{cell}=E^\circ_{cell}-\frac{RT}{2F}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{M^{2+}/M}=E^\circ_{M^{2+}/M}-\frac{RT}{2F}\ln\frac{1}{[M^{n+}]}.$$

Since the EMF of a complete cell is the combination of two halves-cell reactions, it is obtained from the equation (5.14).

For a galvanic cell,

$$Ni(s)\mid Ni^{2+}(aq)\parallel Ag^+(aq)\mid Ag(s)$$

which involves monovalent and divalent ions, the emf expression is written as,

$$E_{cell}=E^\circ_{cell}-\frac{RT}{2F}\ln\frac{[Ni^{2+}(aq)]}{[Ag^+(aq)]^2}$$

For a general electrochemical change of the type,

$$aA+bB\xrightarrow{ne^-}cC+dD$$

the Nernst equation can be written as,

$$E_{cell}=E^\circ_{cell}-\frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

or
$$E_{cell}=E^\circ_{cell}-\frac{RT}{nF}\ln\frac{[Products]}{[Reactants]} \qquad ...(5.18)$$

Substituting the values of constants at 298 K, we get,

$$\frac{RT}{F}=\frac{(8.314JK^{-}mol^{-1})(298K)}{96500\ C\ mol^{-1}}$$

$$=0.0257JC^{-1}=0.0257V$$

Thus at 298 K, the Nernst equation becomes

$$E=E^\circ-\frac{0.0257V}{n}\ln Q$$

For converting the Nernst expression into logarithm, we consider the relationship between log x and ln x *i.e.*, ln x=2.303 log x at 298 K.

$$E=E^\circ-\frac{0.0592V}{n}\log Q \qquad ...(5.19)$$

Using this equation, we can calculate the voltage of a cell if we know the appropriate concentrations (partial pressures, in the case of gases) and E° values for its electrodes.

Exercise 5.8. *Calculate the emf of the following cell at 298 K. E° for the cell is 0.65V.*

$$Sn(s) \mid Sn^{2+}\,(0.15M) \parallel Ag^{+}\,(1.7M) \mid Ag.$$

Solution. The cell reaction is

$$Sn(s)+Ag^{+}(aq) \rightarrow Sn^{2+}(aq)+Ag(s)$$

The Nernst equation for this reaction is

$$E=E^\circ-\frac{0.0592V}{2}\log\frac{[Sn^{2+}]}{[Ag^{+}]^2}$$

$$=0.65V-\frac{0.0592V}{2}\log\frac{0.15}{(1.7)^2}$$

$$=0.65V+0.038V=0.69V.$$

A positive value of greater than 0.65V for the cell tells us that at these concentrations the cell reaction has a greater tendency to take place than at all the standard concentrations. This is in agreement with the Le Chatelier's principle.

Exercise 5.9. *Calculate the EMF of the galvanic cell*

$$Zn(s) \mid Zn^{2+}(aq)(M_1) \parallel Ag^{+}(M_2) \mid Ag(s) \text{ at } 298\text{ K}$$

When 1 $M_1=1.00$ M *and* $M_2=1.00$ M
2 $M_1=0.100$ M *and* $M_2=0.01$ M
3 $M_1=0.012$ M *and* $M_2=0.200$ M

Solution. 1. When the concentration of both the metal ions is the standard one, *i.e.*, 1M, then the cell potential is equal to the standard cell potential. The net reaction for the cell is,

$Zn(s)+2Ag^{+}(aq)\longrightarrow 2Ag(s)+Zn^{2+}(aq)$, and therefore, the Q, the reaction quotient is, $[Zn^{2+}]/[Ag^{+}]^2$

Now the Nernst equation is,

$$E_{cell}=E^\circ_{cell}-\frac{0.0592}{2}\log Q$$

$$E_{cell}=E^\circ_{cell}-\frac{0.0592}{2}\log\frac{1}{1}$$

$$E_{cell}=E^\circ_{cell}=E^\circ_{Ag^{+}/Ag}-E^\circ_{Zn^{2+}/Zn}$$

$$=0.80V-(-0.763V)$$

$$=1.56V$$

2. When $Zn^{2+}=0{\cdot}100M$ and $[Ag^{+}]=0.01M$

$$Q=\frac{0.1}{[0.01]^2}=\frac{1.00\times10^{-1}}{1.0\times10^{-4}}=1.0\times10^{3}=\log Q=3.00$$

For this reaction $n=2$ because the two half-reactions that combine to give the net cell reaction are,

Reduction : $2Ag^{+}(aq)+2e^{-} \longrightarrow 2Ag(s)$
Oxidation : $Zn(s) \longrightarrow Zn^{2+}+2e^{-}$

The cell potential from the Nernst equation will be :

$$E_{cell}=E^{\circ}_{cell}-\frac{0.0592}{2}\log Q$$
$$=1.56-\frac{0.0592}{2}\log(1.0\times10^{3})$$
$$=1.56-0.089=1.471V$$

This may be noted that when $Q=[Zn^{2+}]/[Ag^{+}]^{2}$ is greater than 1, the cell potential is less than the standard cell potential.

3. When $[Zn^{2+}]=1.2\times10^{-2}$ M and
$[Ag^{2+}]=2.00\times10^{-1}$ M

$$Q=\frac{[Zn^{2+}]}{[Ag^{+}]^{2}}=\frac{1.2\times10^{-2}}{4.00\times10^{-2}}=0.30=3.0\times10^{-1}$$

Therefore, $\log Q=-1\log 10+\log 3=-1+0.48=-0.52$

Now, the cell potential, from the Nernst equation will be :

$$E_{cell}=1.56-\frac{0.0592}{2}\times(-0.52)$$
$$=1.56+0.015=1{\cdot}575V$$

This may again be noted that when $Q=[Zn^{2+}]/[Ag^{+}]^{2}$ is less than 1, the cell potential is greater than the standard cell potential.

Equilibrium Constant from the Nernst Equation

The potential of a cell becomes zero when the cell has assumed equilibrium, the reaction quotient, Q is then equal to the equilibrium constant, K_c. For a cell reaction at equilibrium, the Nernst equation can be written as,

$$E=E^{\circ}-\frac{RT}{nF}\ln K_c$$

$$0=E^{\circ}-\frac{RT}{nF}\ln K_c$$

This can be rearranged to,

$$\ln K_c=\frac{nFE^{\circ}}{RT},$$

or
$$\log K_c=\frac{nE^{\circ}}{0.0592\text{ V}}\text{ at 298 }K \qquad ...(5.20)$$

With this equation, we can calculate the equilibrium constant for any oxidation-reduction in aqueous solution from the corresponding standard cell potential.

Exercise 5.10. *Calculate the equilibrium constant for the reaction*

$$Cu\,(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}\,(aq) + 2Ag\,(s)$$

(*The* E°_{cell} *is* $= 0.46$ V)

Solution. Using the equation (5.20),

$$\log K_c = \frac{n\,E^{\circ}_{cell}}{0.0592\ \text{V}}$$

$$= \frac{2\,(0.46\ \text{V})}{0.0592\ \text{V}} = 15.6$$

Therefore $$K_c = \frac{[Cu^{2+}]}{[Ag^{+}]^2} = 4 \times 10^{15}.$$

5.6. GIBB'S FREE ENERGY AND CELL POTENTIAL

When a cell operates, work is done on the surroundings as electrical energy flows through the external circuit. For a reaction taking place in an electrochemical cell, the maximum electrical work done is equal to the voltage E produced by the cell times the amount of electrical charge Q transferred by means of the external circuit through the work producing device (a motor). In other words

$$W_{max., elect} = EQ$$

In the case of the Daniell cell reaction, when 1 mol of Cu is produced, $2F$ of electrical charge (two moles of electrons) are transferred from the zinc electrode to the copper electrode. Thus the maximum work which can be possible by a Daniell cell is

$$W_{max} = 2FE$$

When n number of moles of electrons (faradays) are transferred, then, the

$$W_{max} = nEF$$

It has been established that the free energy decrease for a reaction taking place at constant temperature and pressure is equal to the theoretical maximum amount of work.

$$-\Delta G = W_{max} = nFE$$

or $$\Delta G = -nFE \qquad \text{...(5.21)}$$

Where F is the faraday constant which gives the charge associated with 1 mole of electrons, therefore it will be equal to the product of charge on an electron (1.602×10^{-19} coulomb) and Avogadro's number (6.023×10^{23} electrons per mole of electrons). That is (1.602×10^{-19} coulomb per electron) $\times$ (6.023×10^{23} electrons per mole of electrons), 96500 coulombs per mole of electrons or 96500 C/mol e^- or 96500 CF^{-1}.

Equation (5.21) suggests an important relationship between the free energy of thermodynamics and the cell voltage. Now when the reactants and products are in their standard states, the relationship becomes,

$$\Delta G^\circ = -nFE^\circ$$

Now, the Nernst equation in terms of free energy takes the form, *i.e.*,

$$E = E^\circ - \frac{2.303\ RT}{nF} \log Q$$

$$-\frac{\Delta G}{nF} = -\frac{\Delta G^\circ}{nF} - \frac{2.303\ RT}{nF} \log Q$$

or
$$\frac{\Delta G}{nF} = \frac{\Delta G^\circ}{nF} + \frac{2.303\ RT}{nF} \log Q$$

$$\Delta G = \Delta G^\circ + 2.303\ RT \log Q$$

With the knowledge of the standard free energy, ΔG°, we can calculate the equilibrium constant, by the relation,

$$\Delta G^\circ = -2.303\ RT \log K_c$$

or
$$\Delta G^\circ = -RT \ln K_c$$

For a reaction occurring in the standard galvanic cell of the type,

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

$$\Delta G^\circ = -nFE^\circ_{cell} = -2\ mol \times 96{,}500\ C\ mol^{-1} \times 1.1\ V$$

$$= -212.300\ CV$$

$$= -212.300\ Joule \quad or \quad 212.3\ kJ$$

i.e., $212.3\ kJ\ mol^{-1}$

is the optimum work which could be possible from the cell.

As one goes down the electrochemical series, ΔG° (oxidation) is found to increase and reaches a zero value for H_2/H^+ system. Further down, ΔG° becomes more and more positive. Thus reducing power of metals decreases in this order and reaches a zero value for the H_2/H^+ reference system. Below the H_2/H^+ system, oxidation of metal to metal ion becomes a non-spontaneous process (ΔG°+ve) and instead the reverse process (metal ion to metal reduction process) occurs spontaneously. Hence the M^{n+} ions are good oxidizing agents and oxidizing power increases down the electrochemical series. Thus Ag_2O is a mild oxidizing agent and is used as such in organic chemistry. Cl_2 gas is a still better oxidizing agent.

If one of the three quantities ΔG°, K_c or E°_{cell} is known, each of the other two can be calculated using one or more of these relationships. The following gives the relationships among the algebraic sign of ΔG, the sign of K_c and E and the spontaneity of redox reactions :

Spontaneity of forward reaction	ΔG	K	E_{cell}
Spontaneous	$-$	>1	$+$
Equilibrium	0	0	0
Non-spontaneous	$+$	<1	$-$

5.7. ELECTRODE POTENTIAL AND ELECTROLYSIS

An electrochemical cell in which the electrical energy causes non-spontaneous redox reactions to occur is called an electrolytic cell. This is possible when the external voltage is increased to a value greater than the emf of the cell. At such a stage the electrode reactions are pushed in the opposite direction and the cell starts functioning as an electrolytic cell and the electrolysis takes place. In electrolysis, anions migrate to the anode, where oxidation takes place and cations travel to the cathode, where reduction occurs.

Consider a galvanic cell,

$$Sd(s) \mid Sn^{2+}(1.0\ M) \parallel Cl^-\ (1.0\ M) \mid Cl_2(g) \mid Pt$$

for which

$$E^\circ = E^\circ_{cathode} - E^\circ_{anode}$$
$$= E^\circ_{Cl_2} - E^\circ_{Sn} = 1.36\ V - (-0.14)$$
$$= 1.50\ V$$

The cell reaction is,

$$Sn(s) + Cl_2(g) \longrightarrow Sn^{2+}(aq) + 2Cl^-(aq)$$

When the external voltage exceeds—1·50 V (negative since energy is flowing into the cell) the cell reaction occurs in the reverse direction *i.e.*, electrolysis occurs (Fig. 5.15). Hence, the cell reaction becomes,

$$Sn^{2+}(aq) + 2Cl^-(aq) \longrightarrow Sn\ (s) + Cl_2(g)$$

Thus, the potential needed to effect electrolysis is larger than the voltaic cell potential.

The **overpotential**, as the excess potential is called, is dependent on the particular cell and on the manner in which it is constructed and operated. The overpotentials assume significance when gases are produced during electrolysis. The magnitude of overpotentials vary with the nature and size of the electrode and with the amount of current flowing.

In addition to the **gas over potential, a concentration over potential** is also possible because of the change in concentration of the ions in the neighbourhood of the electrodes. The change in concentration increases the voltaic cell potential which has also to

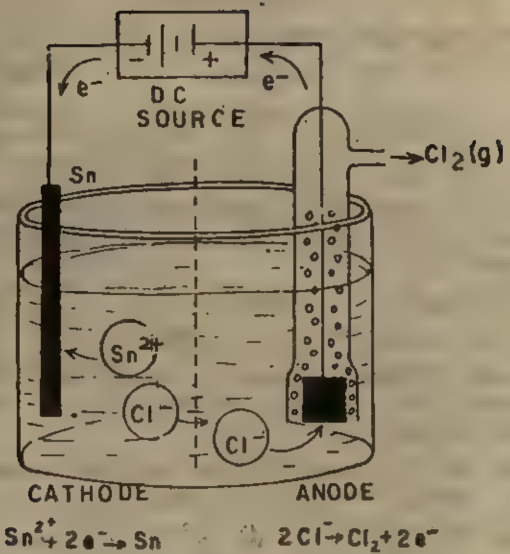


Fig. 5.15. An Sn—Cl_2 galvanic cell becomes an electrolytic cell when the galvanic cell potential is opposed by an external source of electrical energy.

be overcome by the external voltage. Thus, the concentration overpotential is related to the rate of electrolysis and the resulting rate at which the concentrations change.

Consider the electrolysis of sodium chloride solution. Because there are so many species present in this cell, several possibilities exist for both anode and cathode reactions :

Possible anode (oxidation) reactions :

$$2Cl^- \longrightarrow Cl_2(g)+2e^-$$
$$2H_2O \longrightarrow O_2(g)+4H^++4e^-$$
$$4OH^- \longrightarrow O_2(g)+2H_2O+4e^-$$

Possible cathode (reduction) reactions :

$$e^-+Na^+ \longrightarrow Na(s)$$
$$2e^-+2H_2O \longrightarrow H_2(g)+2OH^-$$
$$2e^-+2H^+ \longrightarrow H_2(g)$$

By this it is fully established, that at anode chlorine gas is produced. Thus, the anode reaction is

$$2Cl^- \longrightarrow Cl_2(g)+2e^-$$

And at the cathode hydrogen gas is produced. So either H^+ or H_2O is reduced. Because of the large concentration of H_2O, the cathode reaction is likely to be

$$2e^- + 2H_2O \longrightarrow H_2(g) + 2OH^-$$

The overall cell reaction thus will be,

Anode	$2Cl^- \longrightarrow Cl_2 + 2e^-$	(Oxidation)
Cathode	$2e^- + H_2O \longrightarrow H_2(g) + 2OH^-$	(Reduction)
Cell	$2H_2O + 2Cl^- \longrightarrow H_2(g) + Cl_2(g) + 2OH^-$	

The electrolyte surrounding the cathode shows an increase in OH^- ions concentration. This is because water is easily reduced as is shown by below

$$Na^+(aq) + e^- \longrightarrow Na(s). \qquad E^\circ = -2.1\ V$$

$$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ = 0.83\ V$$

When mercury is used as cathode, the high overvoltage developed by hydrogen at a mercury surface leads to preferential discharge of sodium ions.

At anode, there is a competition between the oxidation of Cl^- ions and that of water. From the E° values,

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O \quad E^\circ = 1.23\ V$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \quad E^\circ = 1.36\ V$$

it appears that water has slightly more chances of getting oxidized.

However, in concentrated solution of NaCl (Cl^- ion is high) oxidation of Cl^- overrides the other two reactions. The same can also be achieved if the anode material is carbon, which leads to a high overvoltage for oxygen (the final product of the discharge of hydroxide ion and that of water)

$$Cl^- \longrightarrow \tfrac{1}{2}Cl_2 + e^-$$

The discharge of OH^- will result in the ionization of more molecules of water to maintain the minute concentration. As a result, the chances of water getting oxidized at the anode are more than that of OH^- ions,

$$2H_2O \longrightarrow 4H^+ + O_2 + 4\,e^-$$

For aqueous solutions which contain ions of comparable concentrations, the ease of dicharge of a particular cation is determined by its position in the electrode potential Table 5.5.

5.8. Some Commercial Cells (Batteries) and Fuel Cell

Cells employed as a source of electrical energy are primarily electrochemical cells. In principle, any redox reaction can be used as the basis of an electrochemical cell. But all the reactions cannot be adopted as the basis of commercial batteries because of certain inherent problems. The most essential requirement of such cells is that their voltage should not vary appreciably during the use.

There are mainly two types of cells :

Primary cells. In these cells, the reaction occurs only once and the battery becomes dead over a period of time *e.g.*, dry cell, mercury cell.

Secondary cells. In these cells, the reaction can be reversed by passing a current through them. This type of recharging makes them suitable for reuse. Lead storage battery, nickel cadmium storage cell, *etc.*, fall under this category.

(*i*) **Daniell Cell** (Fig. 5.16). It consists of a copper vessel which has been divided into two parts by a circular porous pot. Anode made of zinc is immersed in $ZnSO_4$ solution contained in a porous pot. The pot is surrounded by copper sulphate solution. Copper vessel works as cathode. The following reactions occur at the electrodes :

At anode : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

At cathode : $Cu^{2-} + 2e^- \longrightarrow Cu(s)$

The overall reaction is : $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

The emf of the Daniell cell in the beginning is 1.1 volt and this decreases gradually. The emf of the cell depends upon the intensity of the chemical reaction taking place inside the cell. Intensity of the chemical reaction decreases gradually, and hence, emf of the cell decreases gradually. The porous partition allows the migration of ions when the cell is in use. It decreases the diffusion of ions to a large extent when the cell is not in use. This is a practical but less efficient way of preventing mixing of the two electrolytes.

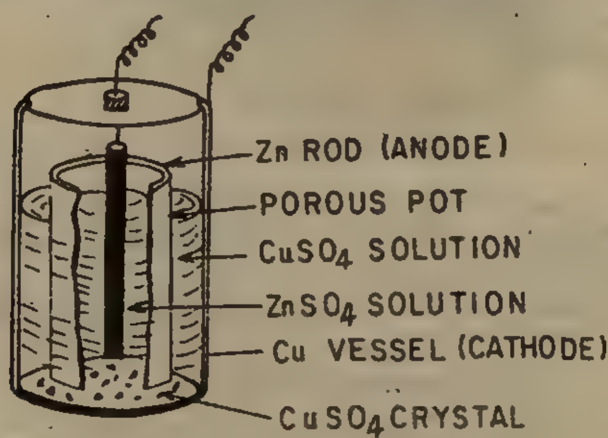


Fig. 5.16. Daniell cell.

(*ii*) **Dry Cell (Leclanche Cell)** (Fig. 5.17). The vessel made of zinc metal serves as an anode, the graphite rod with a brass cap passing through the centre of the cell is the cathode. The space between the electrodes is filled with a moist paste of manganese dioxide, carbon black, zinc chloride and ammonium chloride. The zinc container is lined with porous paper separating zinc from the paste but permits ions to diffuse through it. Its voltage is 1.25V to

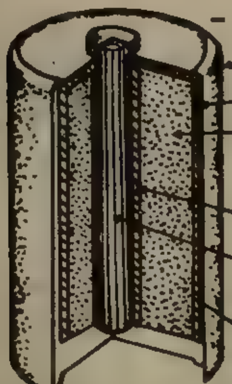


Fig. 5.17. Dry cell.

1.5V. The following reactions take place at electrodes when the cell is in use :

At anode : $Zn(s) \longrightarrow Zn^{2+} + 2e^-$. The cathode reaction is very complex. It seems that MnO_2 is reduced; a plausible reduction reaction is :

At cathode : $2MnO_2(s) + H_2O + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$

An acid-base reaction occurs between OH^- and NH_4^+ ions :

$NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(g) + H_2O$

At times, when a large current is drawn, ammonia produced by the reaction forms an insulating gaseous layer around cathode (carbon) and disrupts the electric current. In the normal course this does not happen as Zn^{2+} ions migrate to the cathode and react with ammonia molecules to form complex ions, such as $[Zn(NH_3)_4]^{2+}$. A so-called 'dead' dry cell can sometimes be put to use again by careful heating which increases the rate of diffusion of Zn^{2+} ions across the cell. During use the zinc casing gets consumed and holes start appearing. These holes are responsible for leakages. Leak proof dry cells have been provided with an extra casing surrounding the zinc vessel.

A cell (EMF=1.35V), developed for hearing aids and other small electrical devices, consists of a moist paste of HgO and KOH between the two electrodes. A lining of porous paper is interposed between zinc anode and the moist paste. The following reactions take place at the two electrodes :

At zinc anode : $Zn+2OH^- \longrightarrow Zn(OH)_2+2e^-$

At carbon cathode : $HgO+H_2O+2e^- \longrightarrow Hg+2OH^-$

The overall reaction : $Zn+HgO+H_2O \longrightarrow Zn(OH)_2+Hg$

(*iii*) **Lead Storage Battery** : The 6 or 12 volt storage battery commonly employed in automobiles consists of 3 or 6 voltaic cells in series (Fig. 5.18). The multiple lead cathode of a fully charged cell is a group of plates filled with lead dioxide. The anode

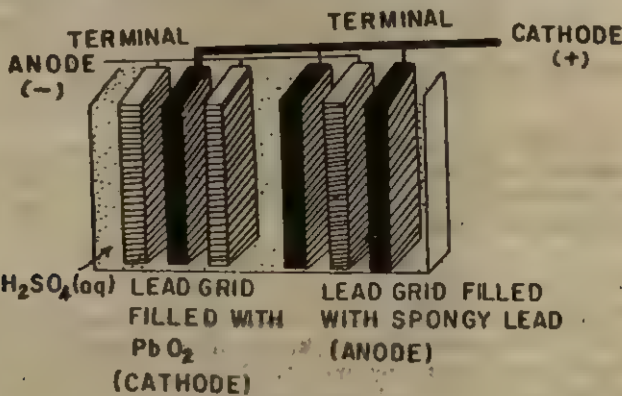


Fig. 5.18. Lead storage battery.

also consists of a group of lead plates, the grids of which are packed with spongy grey lead. These two series of plates are arranged alternately and are immersed in a water solution of sulphuric acid. The electrode reactions are :

At anode : $Pb(s)+SO_4^{2-}(aq) \longrightarrow PbSO_4(s)+2e^-$

At cathode : $PbO_2(s)+4H^+(aq)+SO_4^{2-}+2e^- \longrightarrow PbSO_4(s)+2H_2O$

As current is drawn from the cell, the net reaction is :

Net reaction : $Pb(s)+PbO_2(s)+4H^+(aq)+2SO_4^{2-} \rightarrow PbSO_4(s)+2H_2O$

Thus, solid $PbSO_4$ is produced at both the electrodes, as the cell discharges. Simultaneously, H^+ and SO_4^{2-} or (HSO_4^-) are removed from the solution. Solid $PbSO_4$, produced during reactions, slowly deposits on the plates, partially covering and replacing the lead and lead dioxide. Concentration of H_2SO_4 decreases as the cell discharges. Low density of the electrolyte shows low concentration. The electrode reactions can be reversed by passing an electric cur-

rent through it, and thus, the battery can be recharged. This causes all the reactions to reverse as the cell becomes an electrolytic cell, converting $PbSO_4$ to Pb and to PbO_2 at the respective electrodes.

(*iv*) **Nickel-cadmium cell** : The cell has become very common recently. It powers everything from pocket calculators to cordless trimmers.

It is diagrammed as

$Cd(s) \mid Cd(OH)_2(s) \mid OH^- \mid Ni(OH)_2(s) \mid NiO_2(s)$

As the cell discharges, the following reactions occur

At anode : $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$

At cathode : $NiO_2(s) + 2e^- + 2H_2O(l) \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$

Cell reaction ; $Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$

The cell is rechargeable. The voltage of the cell stays essentially constant until the cell is almost discharged. This has been possible because the ionic concentrations inside the cell do not change as the cell discharges.

Fuel Cell

A fuel cell is a galvanic cell which supply electrical energy as a result of combustion of fuels such as hydrogen, carbon monoxide or methane. The most common and successful fuel cell uses the combustion reaction of hydrogen and oxygen.

Figure 5.19 shows a schematic diagram of a fuel cell which consumes hydrogen and oxygen gases as it operates. The electrodes are porous tubes of carbon impregnated with a catalyst such as platinum, silver or certain transition metal oxides. The gases under pressure are made to pass round the electrodes immersed in concentrated solution of KOH. The diffusion rates of gases into the KOH solution is regulated to achieve maximum efficiency. At the anode of this fuel cell hydrogen is oxidized,

Anode : $H_2(g) + 2OH^- \longrightarrow 2H_2O + 2e^-$

At the cathode oxygen is reduced,

Cathode : $O_2(g) + 4e^- + 2H_2O \longrightarrow 4OH^-$

Thus the overall reaction is the conversion of H_2 and O_2 to water,

Cell reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

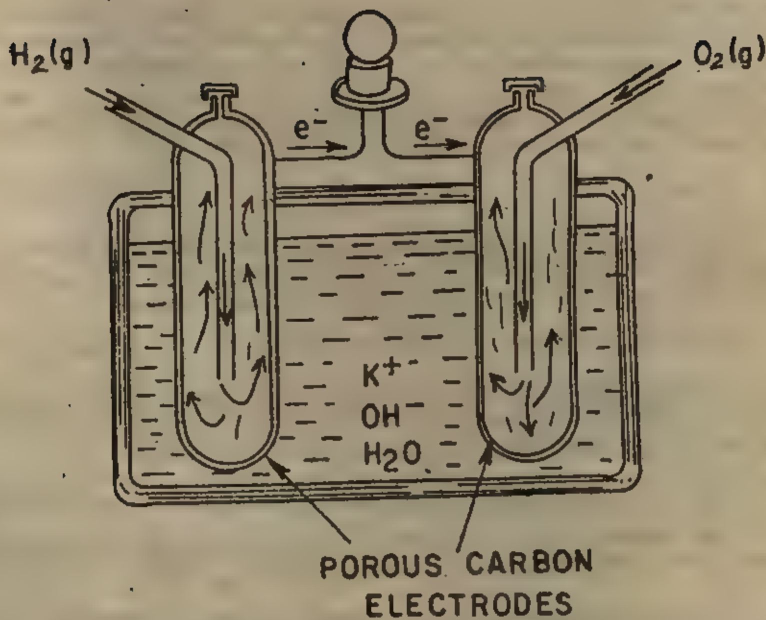


Fig. 5.19. A simple fuel cell.

The cell works continuously as long as the reactants are supplied. In such cells, the reaction of fuel with oxygen is catalyzed to increase the rate of reaction. These cells accomplish the direct conversion of chemical energy into electrical energy. (Conventional electrical power production involves the burning of fuel to produce steam which, in turn, is used to run turbines. This cell has been used for electric power in the Apollo Moon probes. The astronauts used the product of the reaction to supplement their drinking water.

5.9 CORROSION

Around us we come across many metals which react with the substances present in a tmosphere. Silver tarnishes, iron rusts, aluminium oxidizes, copper and brass develop a green coating, lead and even stainless steel slowly lose their luster becasue of corrosion. Metallic parts of ships, automobiles, *etc.*, get corroded.

Ordinary corrosion is the redox process by which metals are oxidized by O_2 in the presence of moisture. The problem of corrosion and its prevention is of both theoretical and practical interest because it is responsible for the loss of crores of rupees every year on this account.

Rusting of iron is the most common type of corrosion. Iron rusts when exposed to damp air or to air saturated water and forms hydrated oxide of variable composition, $Fe_2O_3 \cdot xH_2O$.

It does not form as an adherent film, but rather flakes off, exposing more iron to corrosion. The mechanism of rusting is complex and apparently varies, depending on conditions. It is believed that iron object acts as anode in one region and as cathode in other region. The region of strain (where the metals are most active) acts as anode and oxidation takes place here.

Anode : $Fe(s) \rightarrow Fe^{2+}(aq)+2e^-$ (Oxidation)

The electrons produced at anode then flow along the metal to areas where conditions are favourable for corrosion and reduce oxygen in presence of water. Such regions work as cathodes.

Cathode : $O_2+2H_2O+4e^- \rightarrow 4OH^-$ (Reduction)

If cathodic and anodic regions are close together the OH^- and Fe^{2+} ions diffuse and precipitation of $Fe(OH)_2(s)$ occurs. Iron (II) hydroxide is oxidized by air to rust, hydrated iron (III) oxide :

$$2Fe(OH)_2(s)+\tfrac{1}{2}O_2(aq)+H_2O(l) \rightarrow Fe_2O_3.xH_2O(s) \qquad \text{(Rust)}$$

The system behaves as a galvanic cell with anode and cathode sites removed from each other, as is shown in Fig. 5.20.

Rusting is accelerated by the presence of acids, salts and less active metals, and by elevated temperatures. CO_2 helps rusting by making the solution acidic. NaCl increases the rate of rusting by making water more conducting. NaOH hampers the rusting process be removing hydrogen.

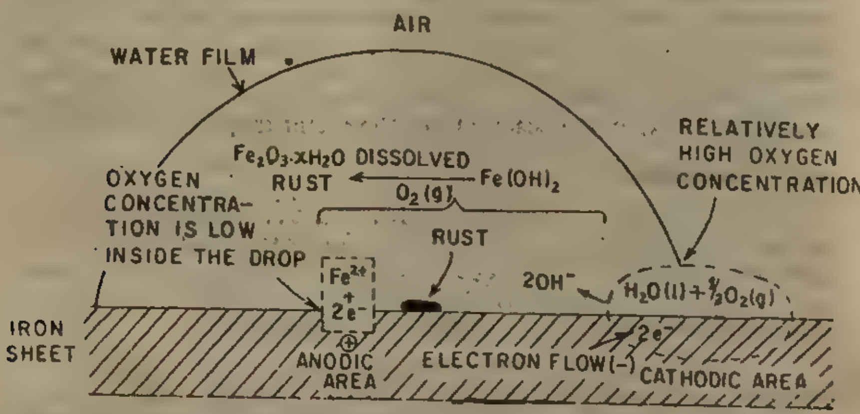


Fig. 5.20. The rusting of iron (Iron in contact with water forms the anode and in contact with air forms the cathode. At the anode iron is oxidized to Fe^{2+}, and at the cathode oxygen is reduced to OH^-.)

Thus, the factors which are involved in the process of rusting are: concentration of oxygen, pH, moisture, irregularities in structure of the metal, presence of electrolyte and its concentration and stray electric currents. The rusting of iron is shown in Fig. 5.20.

With aluminium, the corrosion product oxide forms a strong adherent coating that protects the metal from further corrosion.

Prevention from Corrosion

Corrosion of metals is prevented by covering the surface with a layer of paint, grease or oil. Iron can be rendered passive by the use of a strong oxidizing agent present in paint. A paint containing phosphoric acid is also very effective as it reacts with iron forming an insoluble tenacious film of iron phosphate, $FePO_4$.

Plating with another metal is a usual method of protection, tin plating and galvanizing (coating with zinc) being common examples.

Metal coating is done in two ways : (*i*) electrolysis (Cr, Ni and Cd coatings), (*ii*) Dipping of the objects in a molten metal (Zn and Sn coatings). The galvanized iron does not corrode as long as the coating remains intact. When the protective plating develops cracks zinc metal serves as anode as it is more active than iron and gets oxidized in preference to iron.

It is an example of cathodic protection in which advantage of the reductive potential of zinc is taken.

$$Zn^{2+} + 2e^- \rightarrow Zn(s) \qquad Zn^{2+}/Zn\,E^\circ = -0.76\text{ V}$$
$$Fe^{2+} + 2e^- \rightarrow Fe(s) \qquad Fe^{2+}/Fe\,E^\circ = -0.44\text{ V}$$

The corrosion product of zinc is insoluble zinc hydroxide carborate, $Zn_2(OH)_2CO_3$ which tends to protect zinc from further corrosion by plugging/holes and scratches in zinc.

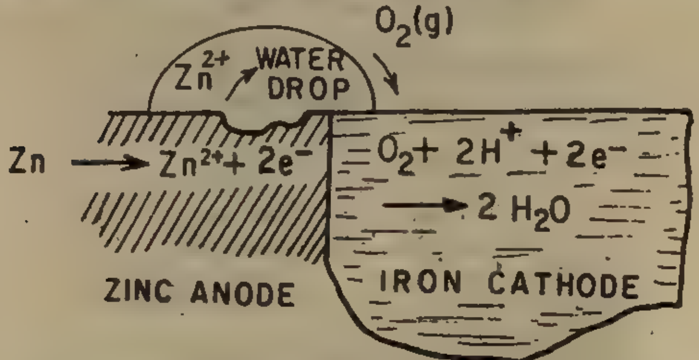


Fig. 5.21. Galvanized iron. Cathodic protection of iron object in contact with zinc is possible by galvanization.

Iron can be coated with copper by electrodeposition from a solution of copper sulphate or with tin by dipping into molten metal. Now if the coating is broken, iron is exposed and iron being more active than both copper and tin is corroded. Here iron corrodes more rapidly than it does in the absence of the tin plate. But tin protects copper in the same way as zinc protects iron.

Electrical (cathodic) protection : Iron articles such as underground pipes, *etc.* are connected with more active metal like magnesium, zinc or aluminium. The more active metal acts as anode and loses electrons in preference to iron. Electrons released are conducted to iron for the reduction of O_2 (or H^+, if the solution is acidic enough).

$$O_2+4H^++4e^- \rightarrow 2H_2O$$

$$\text{Also } O_2+2H_2O+4e^- \rightarrow 4OH^-$$

$$2H^++2e^- \rightarrow H_2$$

As long as the iron acts as cathode, it cannot corrode. Hydrogen ions are discharged at the iron cathode, and thus, prevent the formation of the rust. As long as some of the active metal remains the iron object remains protected. Magnesium and zinc are widely used for protecting objects The metal used for protection is called a sacrificial anode (Fig. 5.22). Since these metals are oxidized quickly, they are replaced from time to time.

Magnesium is widely used in the cathodic protection of buried iron pipelines, canal locks, storage tanks, ships and plumbing

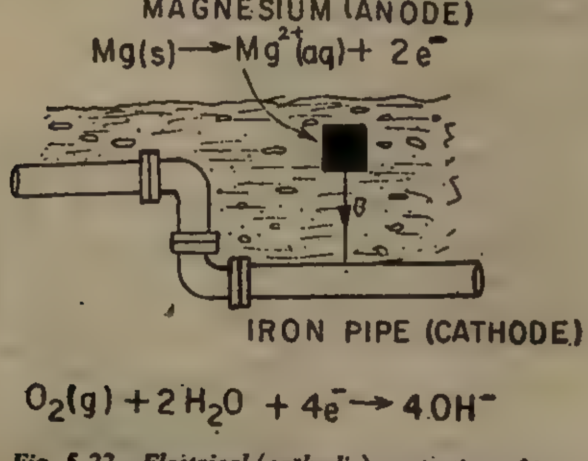


Fig. 5.22. Electrical (cathodic) protection of iron pipes buried underground by using magnesium metal.

systems. In the same way, zinc is employed to protect bronze propellar shafts and rudders of small boats from corrosion by sea water.

Using anti-rust solutions : Corrosion of objects is prevented by using anti-rust solutions, *e.g.*, alkaline phosphate and alkaline chromate solutions. These solutions decrease the rate of rusting by removing H^+ ions. Phosphate ($FePO_4$) provides a tough adherent insoluble coating and protects iron objects.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

5.1 Choose the correct answer of the four alternatives given for the following questions :

(*i*) The unit of molar conductance is

(*a*) $ohm^{-1}\ cm^{-1}$ (*b*) $ohm^{-1}\ cm^2\ mol^{-1}$

(*c*) $ohm^{-1}\ cm^{-1}\ mol^{-1}$ (*d*) $ohm^{-1}\ cm^2$

(*ii*) Which of the following statements is not correct ?

(*a*) The molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the ions produced by that electrolyte.

(*b*) Electrolytic cells are electrochemical cells in which non-spontaneous chemical reactions are made to occur by the forced imput of electrical energy.

(*c*) Galvanic cells are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy.

(*d*) A fuel cell is a source of chemical energy.

(*iii*) Electrolytes, when dissolved in water, dissociate into their constituent ions. The degree of dissociation of an electrolyte increases with the

(*a*) presence of a substance yielding a common ion.

(*b*) increasing concentration of the electrolyte.

(*c*) decreasing temperature.

(*d*) decreasing concentration of the electrolyte.

(*iv*) In the galvanic cell, what allows for the migration of anions between compartments ?

(*a*) the electrodes (*b*) the electrons

(*c*) the external wire (*d*) a salt bridge.

(*v*) In the following electrolytic cell............is............at the anode.

$2\ Cl^-\ (aq) + Fe^{2+}\ (aq) \longrightarrow Fe\ (s) + Cl_2\ (g)$

(*a*) Fe, oxidized (*b*) Cl^-, oxidized

(*c*) Cl^-. reduced (*d*) Fe^{2+}, reduced.

(*vi*) The cell reaction

$$Zn\ (s) + Cu^{2+}\ (aq) \longrightarrow Zn^{2+}\ (aq) + Cu\ (s)$$

is represented by

(*a*) $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$ (*b*) $Cu \mid Cu^{2+} \parallel Zn^{2+} \mid Zn$

(*c*) $Zn \mid Cu^{2+} \parallel Zn^{2+} \mid Cu$ (*d*) $Zn^{2+} \mid Zn \parallel Cu \mid Cu^{2+}$

(*vii*) At equilibrium, for an electrochemical cell

(*a*) E is zero (*b*) $\log K_c$ is zero

(*c*) ΔG is negative (*d*) E is negative.

(*viii*) A solution containing one mole per litre each of $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$ is electrolyzed using inert electrodes. E° in volt (reduced potential) are : $Ag^+/Ag = 0{\cdot}80$, $Cu^{2+}/Cu = 0{\cdot}34$, $Hg_2^{2+}/2\,Hg = 0.79$, $Mg^{2+}/Mg = -2{\cdot}37$. With increasing voltage, the sequence of deposition of metals on the cathode will be :

(*a*) Ag, Hg, Cu, Mg (*b*) Mg, Cu, Hg, Ag

(*c*) Ag, Hg, Cu (*d*) Cu, Hg, Ag (IIT 1984)

(*ix*) The electric charge for electrode deposition of one gram equivalent of a substance is :

(*a*) one ampere for one second

(*b*) 96,500 coulombs per second

(*c*) one ampere for one hour

(*d*) charge on one mole of electrons. (IIT 1984)

(*x*) The reaction $\frac{1}{2}\,H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Cl^-(aq) + Ag(s)$ occurs in the galvanic cell

(*a*) Ag | AgCl(s) | KCl solution | Ag NO_3(aq)/Ag

(*b*) Pt | H_2(g) | HCl solution | $AgNO_3$(aq) | Ag

(*c*) Pt | H_2(g) | HCl solution | AgCl(s) | Ag

(*d*) Pt | H_2(g) | KCl solution | AgCl(s) | Ag. (IIT 1985)

(*xi*) When a lead storage battery is discharged,

(*a*) SO_2 is evolved

(*b*) lead is formed

(*c*) lead sulphate is consumed

(*d*) sulphuric acid is consumed. (IIT 1987)

(*xii*) The standard reduction potential, E° for the half-reactions are as, (IIT 1988)

Zn^{2+}/Zn $E^\circ = +0.76$ V

Fe^{2+}/Fe $E^\circ = -0.41$ V

The emf for the cell reaction $Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$ ...is

(*a*) -0.35 V (*b*) 0.35 V

(*c*) $+1.17$ V (*d*) -1.17 V.

5.2. Fill in the blanks with appropriate words :

(*i*) ΔG for an electrolytic cell is............

(*ii*) Each galvanic cell produces a............which is the............of the potentials of its single electrodes.

(*iii*) The voltage produced by a cell measures the...............of its cell ....

(*iv*) The Nernst equation permits calculations of cell voltages when reactants and products are................

(*v*) The free energy change, ΔG of a reaction and its standard free energy change ΔG°, are related by...............

(*vi*) In voltaic cell, oxidation occurs at the............from which electrons flow through the external circuit to the...............

(*vii*) ....flow toward the anode through a salt bridge to maintain electrical balance.

(*viii*) For a voltaic cell, W_{max} ΔG=...............

(*ix*) The potential at which electrolysis occurs, is often............than the voltaic cell potential because of...............

(*x*) Use of zinc coating to protect iron from corrosion is called............

5.3. **Choose True (T) and False (F) from the following statements :**

(*i*) The negative sign for E°, r [illegible] s the fact that Zn^{2+} is more difficult to reduce than H^+.

(*ii*) The movement of ions is responsible for the flow of electric current through solution.

(*iii*) Reduction always takes place at the anode and oxidation always takes place at the cathode.

(*iv*) The chemical reactions that occur at the electrodes during electrolytic conduction constitute electrolysis.

(*v*) The quantity of electricity that must be supplied to a cell in order to deliver 1 mol of electrons is equal to one coulomb.

(*vi*) The salt bridge permits a continuous electron flow through the solution as a result of oxidation-reductions taking place at the electrodes.

(*vii*) Electrode potential depends upon the concentration of ions in the cell.

(*viii*) A piece of metallic zinc on inserting into a solution of copper sulphate does not experience any chemical change.

(*ix*) The thermodyramic criterion for spontaneity of a chemical reaction occurring at constant temperature and pressure is that ΔG has to be a negative quantity.

(*x*) Standard cell potential is a measure of the equilibrium constant for the cell reaction.

SHORT ANSWER QUESTIONS

5.4. (*i*) What is meant by electrolysis and by an electrolyte ?

(*ii*) How does ionic conduction differ from electronic conduction ?

(*iii*) Which of the following will be oxidized by an acidic solution of $K_2Cr_2O_7$? Answer on the basis of electrochemical series :

F^-, Cl^-, Br^-, I^-, Hg_2^{2+}, Mn^{2+}, Fe^{2+}, H_2S.

(*iv*) Arrange the following metals in the order in which they displace each other from solution : Al, Cu, Fe, Mg and Zn.

(*v*) Not all metals can be deposited electrolytically from aqueous solutions. Comment on the statement using the electrolysis of

(*a*) molten sodium chloride, and

(*b*) aqueous solution of sodium chloride as examples.

(*vi*) What happens when the lead accumulator is charged ? Explain through diagram.

(*vii*) Predict from the table of standard electrode potential whether the following reactions occur :

(*a*) Will Mg(s) displace Sn^{2+} from aqueous solution ?

(*b*) Will copper (s) reduce Ag^+ ion aqueous solution ?

(*c*) Pb^{2+} (aq)+2 Ag(s) $\longrightarrow$ 2 Ag^+ (aq)+Pb (s)

(*d*) 2 Ag^+ (aq)+Pb(s) $\longrightarrow$ 2 Ag (s)+Pb^{2+} (aq)

(*e*) Will copper(s) dissolve in 1M HCl ?

(*f*) Will Zn(s) displace Al(aq) from solution ?

(*viii*) The following cell has $E^\circ = 0.66$ V. The Fe^{2+}/Fe electrode is the anode. Fe | Fe^{2+} ‖ Cl^- | AgCl/Ag. Calculate its E° value.

(*ix*) Calculate the emf of the cells formed by the various combinations of the following standard half-cells. (concentration is 1 mol L^{-1})

1. Zn(s) | Zn^{2+} (aq)	2. Cr(s) | Cr^{3+} (aq)
3. Cu(s) | Cu^{2+} (aq)	4. Ni(s) | Ni^{2+} (aq)
5. Cu(s) | Cu^{2+} (aq)	6. Ag(s) | Ag^+ (aq)

(*x*) Give the anodic and cathodic reactions for the following. Indicate the positive terminal in each case :

1. Zn(s) | Zn^{2+} ‖ Br^-, Br_2(g) | Pt(s)
2. Cr(s) | Cr^{3+} ‖ I^-, I_2 | Pt(s)
3. Pt(s) | H_2(g) ‖ H^+(aq) | Cu^{2+} | Cu(s).

(*xi*) Calculate the emf of the cell

$$Pb(s) \mid Pb(NO_3)_2\ (M_1) \parallel HCl\ (M_2) \mid H_2(g) \mid Pt(s)$$

When $M_1 = 0{\cdot}1$ M ; $M_2 = 0{\cdot}2$ M and $P_{H_2\,(g)} = 1$ atm.

TERMINAL QUESTIONS

5. 1. Explain what is meant by (*a*) the electrolytic conductivity, and (*b*) the molar conductivity of an electrolyte. Outline how (*a*) and (*b*) could be found. Draw curves to show how (*a*) and (*b*) vary with dilution for a strong and a weak electrolyte.

5. 2. Describe an experimental method for finding the molar conductivity at infinite dilution Λ_m^∞ of an aqueous solution at 298 K.

5. 3. Comment on the following terms :

(*i*) weak and strong electrolytes, and

(*ii*) electrolysis

5. 4. What is Kohlrausch's law of independent migration of ions ? Illustrate.

5. 5. How does the molar conductivity vary with concentration ? Explain by taking examples of weak and strong electrolytes.

5. 6. What is a galvanic cell ? How does it differ from electrolytic cell ?

5. 7. State Faraday's Law of electricity ? What is a faraday of electricity ?

5. 8. Why is the hydrogen ion rather than the Na^+ ion reduced at the cathode during the electrolysis of aqueous sodium chloride ? What is the source of H^+ ion ?

5. 9. Define standard electrode potential and outline the essential features of a method for measuring the standard electrode potential of zinc ion/zinc electrode.

5.10. Explain how the electromotive series was experimentally established ? List some uses of the electromotive force series.

5.11. What is the origin of the value zero for the standard hydrogen electrode ?

5.12. Explain how the Nernst equation is used in electrochemistry.

5.13. (*a*) Describe the construction of the dry cell and give its net reaction.

(*b*) Give equations for the net reactions at the two different kinds of plate in a lead storage battery.

5.14. In what ways the standard cell potentials are related to equilibrium constant and free energy. Derive the expressions with the help of the Nernst equation.

5.15. What is corrosion ? What are the factors which affect corrosion ? Suggest a few protective measures.

5.16. Galvanized iron has a coating of zinc metal to protect the iron from rusting. Explain how this works.

5.17. Using the standard electrode potentials, relate the differences between the chemical properties of the elements mentioned below to the differences between the standard electrode potentials of the following systems.

(*i*) $K^+(aq) \mid K(s)$ (*ii*) $Mg^{2+}(aq) \mid Mg(s)$

(*iii*) $Ca^{2+}(aq) \mid Ca(s)$ (*iv*) $Fe^{3+}(aq) \mid Fe(s)$

(*v*) $Cu^{2+}(aq) \mid Cu(s)$ (*vi*) $Cl_2(g) \mid Cl^-(aq)$

5.18. Two half-cells are

(*i*) $Co^{2+}(aq)(1M) \mid Co(s)$ (*ii*) $Cl_2(g)$ (1 atm) $\mid Cl^-(aq)(1M) \mid Pt$

State which will be the positive and which the negative electrode when the two half-cells are connected. Give the equation for the cell reaction. If the emf of the cell is 1.63V what will be $E°$ for the cobalt half-cell ?

(Ans. −0·46V)

5.19. Calculate the standard emf's of the following cells at 298K :

(*i*) $Zn(s) \mid Zn^{2+}(aq) \parallel Pb^{2+}(aq) \mid Pb(s)$

(*ii*) $Ag(s) \mid Ag^+(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

(*iii*) $Fe(s) \mid Fe^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

(*iv*) $Sn(s) \mid Sn^{2+}(aq) \parallel Ag^+ \mid Ag(s)$

(Ans. (*i*) +0.63V (*ii*) −0.46V (*iii*) +0.78V (*iv*) +0.94V)

5.20. Find the molar conductivity at infinite dilution, Λ_m^∞ for AgBr. Values of Λ_m^∞ /ohm^{-1} m^2 mol^{-1} are KBr, $1{\cdot}52 \times 10^{-2}$; KNO_3, $1{\cdot}45 \times 10^{-2}$; $AgNO_3$, $1{\cdot}33 \times 10^{-2}$.

Explain the principle on which the calculation is based.

[(Ans. $1{\cdot}40 \times 10^{-2}$ ohm^{-1} m^2 mol^{-1})

5.21. Calculate the Gibb's free energy change and the equilibrium constant for the following reaction at 298K :

$$Zn(s) + Cu^{2+}(aq)\ (0{\cdot}20M) \rightarrow Zn^{2+}(aq)(0.50M) + Cu(s)$$

$E°$ for this type of cell under standard conditions is 1·10V.

$E°_{Cu^{2+},Cu} = -0.34V$, $E°_{Zn^{2+},Zn} = -0.76V$

(Ans. $\Delta G = -211.26$kJ

$K_c = -1.0 \times 10^{37}$)

5.22. Calculate E for the oxidation of Cl^- at 0.010M to Cl_2 at 5.0 atm

$2Cl^-(1.0M) \rightleftharpoons Cl_2(1\ atm)+2e^-$ $\qquad E^\circ=-1.36V$

(Ans. $E^\circ=-1.5V$)

5.23. For the Daniell cell

$Zn/Zn^{2+}(0.5\ mol\ dm^{-3}) \| Cu^{2+}(0.1\ mol\ dm^{-3}) | Cu,$

Write down the cell reaction and compute the cell EMF and free-energy change at 298 K. (Ans. 1.079V, 208.225 kJ)

5.24. For the cell

$Li | Li^+(0.5\ mol\ dm^{-3}) \| F^-(0.01\ mol\ dm^{-3}) | Pt(F_2)$

Write down the cell reaction and compute the cell EMF and free-energy change at 800K. (Ans. 6.280V, 1211.914 kJ)

5.25. Calculate the half-cell potential at 298 K for the reaction

$Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$, if $[Cu^{2+}]$ is 2.0 mol dm^{-3}

and E° is +0.34V. (Ans. 0·3489V)

ANSWERS TO SELF ASSESSMENT QUESTIONS

5.1. (*i*) b (*ii*) d (*iii*) d (*iv*) d (*v*) b
(*vi*) a (*vii*) a (*viii*) c (*ix*) d (*x*) c
(*xi*) d (*xii*) b

5.2. (*i*) positive (*ii*) voltage, sum
(*iii*) spontaneity reaction (*iv*) not in their standard states,
(*v*) $\Delta G=\Delta G^\circ+RT\ ln\ Q$ (*vi*) anode, cathode
(*vii*) anions (*viii*) $-nFE$
(*ix*) larger over potential (*x*) galvanization

5.3. (*i*) T (*ii*) T (*iii*) F (*iv*) T
(*v*) F (*vi*) F (*vii*) T (*viii*) F
(*ix*) T (*x*) T

5.4. (*i*) Electrolysis is a process in which electrical energy is used to effect a chemical change. An electrolyte is a chemical compound which in molten form or when dissolved in a solvent will carry an electric current.

(*ii*) In ionic conduction, the electrical current is carried by ions whereas in electronic conduction it is carried by electrons.

(*iii*) Br^-, I^-, Hg_2^{2+}, Fe^{2+} and H_2S

(*iv*) Mg, Al, Zn, Fe, Cu

(*v*) The metal deposited at the cathode depends upon its position in the electrochemical series.

In the electrolysis of molten sodium chloride there is only one cation present and so sodium is discharged.

$$Na^+(l)+e^- \rightarrow Na(s)$$

However, during the electrolysis of aqueous sodium chloride, two cations are present,

$Na^+(aq)$ and $H_3^+O(aq)$. $H_3^+O(aq)$ is lower in the electrochemical series and so the following cathode reaction takes place

$$2H_3^+O(aq)+2e^- \rightarrow H_2(g)+2H_2O(l)$$

(vi)

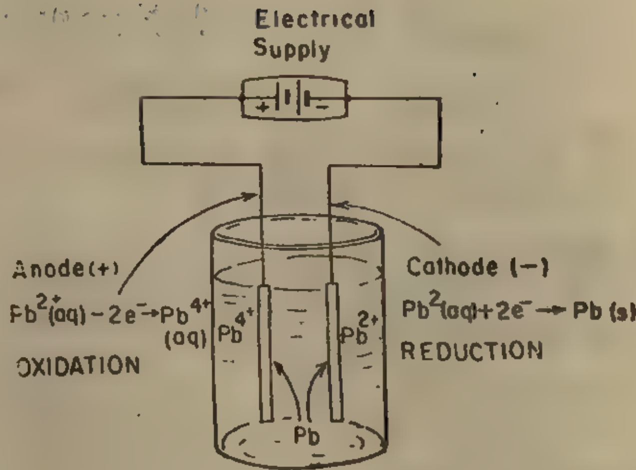


Fig. 5.23

(vii) (a) Yes, (b) Yes (c) No (d) Yes
(e) No (f) No

(viii) Since $E^\circ_{cell} = E_{Cathode} - E_{anode}$

$$0.66 = 0.22V - E^\circ_{anode}$$

$$E^\circ_{anode} = 0.22V - 0.66V = -0.44V$$

(ix) By combining (2) and (4)

i.e., $E^\circ Ni^{2+}/Ni = -0.425V$ and $E^\circ Zn^{2+}/Zn = -0.76V$

$$E_{cell} = E_{cathode} - E_{anode}$$
$$= -(0.25) - (-0.76)$$
$$= -0.25 + 0.76 = 0.51V$$

By combining (2) and (5)

$E^\circ_{CO^{2+}/CO} = -0.28\ V : E^\circ\ _{Cr^{3+}/Cr} = -0.74V$

$$E_{cell} = E_{cathode} - E_{anode}$$
$$= -0.28 - (-0.74)$$
$$= -0.28 + 0.74 = 0.46V$$

By combining (3) and (6)

$D^\circ\ Ag^+/Ag = 0.80V\ E^\circ\ Cu^{2+}/Cu = 0.34V$

$$E_{cell} = E_{cathode} - E_{anode}$$
$$= 0.80 - 0.34$$
$$= 0.46V$$

(x) Reaction at anode

1. $Zn(s) \longrightarrow Zn^{2+} + 2e^-$
Positive terminal

Reaction at cathode

$Br_2 + 2e^- \longrightarrow 2Br^-$

$Br^- \mid Br_2 \mid Pt(s)$

2. $2Cr(s) \longrightarrow 2Cr^{3+}+6e^-$
   Positive terminal

   $3I_2+6e^- \longrightarrow 6I^-$
   $I^- \mid I_2 \mid Pt(s)$

3. $H_2(g) \longrightarrow 2H^++2e^-$
   Positive terminal

   $Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$
   $Cu^{2+} \mid Cu(s)$

Cell reaction : 1. $Zn(s)+Br_2(g) \longrightarrow Zn^{2+}(aq)+2Br^-(aq)$

2. $2Cr(s)+3I_2(g) \longrightarrow 2Cr^{3+}(aq)+6I^-(aq)$
3. $Cu^{2+}(aq)+H_2(g) \longrightarrow Cu(s)+2H^+(aq)$

(*xi*) The cell reaction

$Pb(s)+2H^+(aq) \longrightarrow Pb^{2+}(aq)+H_2(g)$

$E_{cell} = E_{right} - E_{left} = E_{H_2} - E_{Pb}$

By using the Nernst's equation,

$$E_{cell} = {}^\circ E_{H_2} + \frac{0.059}{2} \log [H^+]^2 - \left[E^\circ_{Pb} + \frac{0.059}{2} \log [Pb^{2+}]\right]$$

Substituting the value for $E^\circ_{H_2}$ and E°_{Pb} from the Table 5.5

$$E = 0-(-0.13)+\frac{0.059}{2} \log \frac{[0.2]^2}{[0.1]}$$

$$= 0.13-0.0112 = 0.1183V$$

□ □

UNIT 6

Chemical Kinetics

"In science men have discovered an activity of the highest value in which they no longer, as in art, depend for progress upon the appearance of continually greater genius, for in science the successors stand upon the shoulders of their predecessors."

—BERTRAND RUSSELL

UNIT PREVIEW

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Understand what is meant by the terms reaction rate and kinetics.
2. Understand ways to measure reaction rate.
3. Write expressions for reaction rate.
4. Know the meaning of rate constant.

5. Understand the meaning of "Order of reaction" and be able to calculate, from the rate law for a reaction, what the order of a reaction is in terms of a particular reagent or for the overall reaction.
6. Calculate the change in the rate of a reaction with a specific change in the concentration(s) of the reactant(s), if the rate law is known.
7. Learn the dependence of reaction rate with temperature.
8. Determine activation energy of a reaction.
9. Understand photochemical reactions.
10. Study fast reactions.
11. Able to illucidate reaction mechanism.

6.1. INTRODUCTION

The word '**kinetic**' is obtained from the Greek word '**KINETICKOS**' *i.e.*, 'to move' and the study of the kinetics of chemical reactions provides two vital informations—rates or speeds with which chemical reactions proceed and the path followed by these reactions. Knowledge of reaction rates or speed of a reaction has direct impact on chemical industries.

The qualitative aspect of these studies has already been discussed in the Unit 11 of class XI book. In this unit we shall deal with the quantitative aspect of the rates of a variety of chemical reactions and the conditions controlling them. We shall also try to employ the rate data to understand the path followed by these reactions—**Reaction Mechanism.**

6.2. RATE OF REACTION

6.2.1. Meaning of Reaction Rate

Reactions proceed with different rates, some are called fast reactions, some are slow reactions which take considerable time to change into products. Slow and fast reaction is only a qualitative way to describe the meaning of reac .on rate. In order to understand the exact meaning of the rate of reaction, it is necessary to know the meaning of reaction rate quantitatively. Consider the reaction :

$$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$$

Since the other gases are colourless, the colour change indicates the number of moles of NO_2 that have reacted during the time interval. The quotient, number of moles reacted divided by time interval, is called the rate of the reaction :

$$\text{Rate} = \frac{\text{quantity of } NO_2 \text{ consumed}}{\text{time interval}}$$

$$= \text{quantity of } NO_2 \text{ consumed per unit time}$$

We observe it is not only the NO_2 but also CO which is consumed thus, we can express the rate of the reaction in terms of the rate of consumption of either CO or NO_2. As CO and NO_2 are consumed, simultaneously CO_2 and NO are being formed. Equally

well, we can express the rate of reaction in terms of the appearance of either product CO_2 or NO. The one which is to be used, depends upon the fact which is convenient to measure. If it is convenient to measure the production of CO_2, we can express the rate in the form

$$\text{Rate} = \frac{\text{quantity of } CO_2 \text{ produced}}{\text{time interval}}$$

$$= \text{quantity of } CO_2 \text{ produced per unit time}$$

Thus "the rate of a chemical reaction is the change per unit time of the concentration of either reactants or products in the reaction".

When we plot these concentrations with time, a graph (Fig 6.1) is obtained. An inspection of these curves reveals that the rate of the reaction changes with time.

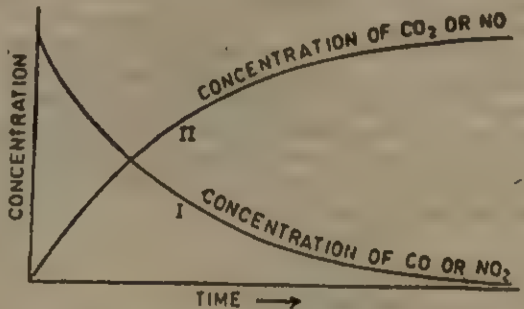


Fig. 6.1. Change in concentration of reactants and products with time.

It can be seen from these curves, that at the start of the reaction, the concentration of either reactant is quite high which decreases rapidly with time (Fig. 6.1, curve I). On the other hand, the concentration of products which was nil at the beginning of the reaction increases quite fast with time (Fig. 6.1, curve II).

In general, the rate (or speed) of any chemical reaction can be expressed as the ratio of the change in concentration of a reactant (or product) to time interval. Mathematically,

$$\text{Rate} = \frac{\text{final concentration of reactant} - \text{initial concentration of reactant}}{\text{time interval}} \quad \text{...(6.1)}$$

$$= \frac{\text{final concentration of product} - \text{initial concentration of product}}{\text{time interval}} \quad \text{...(6.2)}$$

$$= \frac{C_f - C_i}{\text{time interval}} \quad \text{...(6.3)}$$

here, C_f and C_i are the final and initial concentrations respectively (either reactant or product).

Now let us consider a simple reaction

$$R \longrightarrow P.$$

i.e., reactant, R changes into product, P the rate of this reaction can be calculated by substituting the concentration of either R or P at different interval of times in the equation (6.3). On substituting these values in the equation (6.3), we get

$$\text{Rate} = \frac{[R]_f - [R]_i}{\text{time interval}} = \frac{\Delta[R]}{\Delta t} \qquad ...(6.4)$$

or $$\text{Rate} = \frac{[P]_f - [P]_i}{\text{time interval}} = \frac{\Delta[P]}{\Delta t} \qquad ...(6.5)$$

On substituting the experimental values (the rate of reaction is always determined experimentally) of the concentrations, we find that the rate as calculated from the equation (6.4) comes out to be negative. **The rate of a reaction is always positive.** Thus, whenever the rate is expressed in terms of the concentration of reactants, **a minus sign is always put before the expression.** This minus sign is because the concentration of the reactant decreases with time. Thus, the correct expressions for expressing the rate of a reaction are

$$\text{Rate} = -\frac{\Delta[\text{reactant}]}{\Delta t} \qquad ...(6.6)$$

or $$\text{Rate} = +\frac{\Delta[\text{product}]}{\Delta t} \qquad ...(6.7)$$

Consider a general reaction : $A + 2B \longrightarrow C + 3D$

The rate of this hypothetical or any other reaction can be expressed more specifically as the rate at which one of the reactants disappears or a product appears. Mathematically the rate can be written as,

The rate of disappearance of the reactant, $A = -\frac{\Delta[A]}{\Delta t}$ ...(6.8)

Similarly if the rate of reaction is expressed as disappearance of reactant B, the rate could be,

$$\text{Rate} = -\frac{\Delta[B]}{\Delta t} \qquad ...(6.9)$$

Since two moles of B react with one mole of A, thus, concentration of B which disappears in a certain period of time would be just the double of the concentration of the reactant, A, which disappears in the same period of time. Thus, the **correct expressions for the rate of this reaction** are

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{\Delta[B]}{\Delta t} \qquad (6.10)$$

In a similar fashion, one can write for the products :

$$\text{Rate}=\frac{\Delta[C]}{\Delta t}=\frac{1}{3}\;\frac{\Delta[D]}{\Delta t} \qquad ...(6.11)$$

where $\Delta[C]$ and $\Delta[D]$ represent the change in molar concentrations of products C and D respectively during the time interval Δt. The positive sign in the above expression denotes that the $\Delta[C]$ and $\Delta[D]$ increased as time passed. From equations (6 10) and (6·11), we can express the rate of reaction :

$$\text{Rate}=-\frac{\Delta[A]}{\Delta t}=\frac{1}{2}\;\frac{\Delta[B]}{\Delta t}$$

$$=\frac{\Delta[C]}{\Delta}=-\frac{1}{3}\;\frac{\Delta[D]}{\Delta t} \qquad ...(6.12)$$

The general way in which the **rate of a reaction can be expressed is the quotient of concentration change with time, divided by the coefficient of the particular species in the balanced chemical equation. The minus sign is given in the equation if the rate is expressed as the change in the concentration of reactant, and plus sign is given in the equation when the concentration change of either product is considered.**

Units of Reaction Rate

Reaction rate has units of concentration divided by time. Concentration is expressed in moles per cubic decimetre, time may be expressed in seconds, minutes, hours, days or years. Thus, the units of reaction rate would be

$$\frac{\text{mol}}{\text{dm}^3-\text{s}},\ \frac{\text{mol}}{\text{dm}^3-\text{min}},\ \frac{\text{mol}}{\text{dm}^3-\text{hr}},\ \frac{\text{mol}}{\text{dm}^3-\text{yr}}$$

Consider the decomposition of nitrogen pentoxide at 330 K

$$2N_2O_5(g) \longrightarrow 4NO_2(g)+O_2(g)$$

We can express the rate of this decomposition using the following rate expressions

$$\text{Rate}=-\frac{1}{2}\;\frac{\Delta[N_2O_5]}{\Delta t}$$

or $$\text{Rate}=\frac{1}{4}\;\frac{\Delta[NO_2]}{\Delta t}$$

or $$\text{Rate}=\frac{\Delta[O_2]}{\Delta t}$$

Reaction rate $=\frac{1}{2}$ (rate of disappearance of N_2O_5)

$=\frac{1}{4}$ (rate of formation of NO_2) or

$=$(rate of formation of O_2)

6.2.2. To Write Rate Expressions

To write correct and equivalent rate expressions for a chemical reaction, one must follow the following rules :

(*i*) "The rate of a reaction is given by the change in concentration divided by the time needed for the change. Either of the reactants or the products can be utilised to specify the rate. (*ii*) Since the concentration of reactant decreases with time the minus sign is put before Δ[reactant] whereas the change in concentration of product, Δ[product] is positive. (*iii*) The different expressions for the rate can be made equivalent by dividing the rate expressions by the stoichiometric coefficients present in the balanced chemical equation.

For the reaction

$$N_2(g)+3H_2(g) \longrightarrow 2NH_3(g)$$

$$\text{rate of reaction}=-\frac{\Delta[N_2]}{\Delta t}=-\frac{1}{3}\frac{\Delta[H_2]}{\Delta t}=\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

Exercise 6.1. *Combustion of propane proceeds as,*

$$C_3H_8+5O_2 \longrightarrow 3CO_2+4H_2O$$

Write the rate of the reaction in terms of (i) rate of formation of CO_2, (ii) rate of disappearance of C_3H_8, (iii) rate of disappearance of O_2, and (iv) rate of formation of water.

Solution. The different expressions for the rates are :

$$\text{Rate of formation of } CO_2=\frac{1}{3}\frac{\Delta[CO_2]}{\Delta t}$$

$$\text{Rate of disappearance of } C_3H_8=-\frac{\Delta[C_3H_8]}{\Delta t}$$

$$\text{Rate of disappearance of } O_2=-\frac{1}{5}\frac{\Delta[O_2]}{\Delta t}$$

$$\text{Rate of formation of } H_2O=\frac{1}{4}\frac{\Delta[H_2O]}{\Delta t}$$

The positive sign shows that the concentrations of CO_2 and H_2O (*i.e.*, of the products) are increasing with time while the negative sign in the other two cases shows that the concentrations of C_3H_8 and O_2 (*i.e.*, of the reactants) are decreasing with time.

To equate the four rates, each rate is divided by the coefficient of the corresponding substance in the balanced chemical equation.

6.2.3. Ways to Measure Reaction Rate

To determine the rate of a reaction, change in the concentrations of either reactant or product is measured with time. To measure the concentration at any instant, first the reaction is to be stopped which is done by pouring the reaction mixture in ice cold water. At such a low temperature the rate of reaction can be

assumed to be almost zero, *i.e.*, the reaction has completely stopped, this process is called **'quenching the reaction'**.

Reaction rates are determined by measuring the rate at which some property of the reaction changes. Some important properties which have been studied are colour, volume of the system, pressure, rotation of polarized light, mass of reactant consumed or precipitate formed, and pH. The examples in the Table 6.1 illustrate how some of these properties are used.

TABLE 6.1. Illustrative examples of properties used to determine the concentration

S. No.	Property which changes with time	Sample reaction
(*i*)	Colour	$N_2O_4(g) \longrightarrow 2NO_2(g)$
(*ii*)	Volume/pressure	$N_2O_5(g) \longrightarrow 2NO_2(g)+\frac{1}{2}O_2(g)$ $CaCO_3(s) \longrightarrow CaO(s)+CO_2(g)$
(*iii*)	Rotation of polarized light	Inversion of sucrose
(*iv*)	mass	$Zn(s)+2HCl(l) \longrightarrow ZnCl_2(aq)+H_2(g)$
(*v*)	pH	$CH_3COOC_2H_5(aq)+H_2O(l) \rightarrow CH_3COOH(aq) + C_2H_5OH(aq)$

6·2.4. Average Rate of Reaction

The rate of reaction over a time interval is usually referred to as the average rate of reaction. It can be determined as follows :

$$\text{Rate}=\frac{[\text{reactant}]_f-[\text{reactant}]_i}{\text{time interval}}$$

or
$$\text{Rate}=\frac{[\text{product}]_f-[\text{product}]_i}{\text{time interval}}$$

Exercise 6·2. *If it takes 1 nanosecond for hydrogen ions with concentration of* 1×10^{-3}M *to disappear, what is the average rate of the reaction ?*

Solution.
$$\text{Rate}=\frac{\text{concentration change}}{\text{time}}$$
$$=\frac{1\times10^{-3}\text{ mol L}^{-1}}{1\times10^{-9}\text{s}}$$
$$=1\times10^{6}\text{ mol L}^{-1}\text{ s}^{-1}$$

Exercise 6.3. *In a given reaction :* $CH_4(g)+2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$ *at 400K it is observed that the oxygen pressure falls from 0.50 to 0.10* atm *in 30* min. *Calculate the average rate of the reaction in* (*i*) *atmospheres per minute, and* (*ii*) *molarity per second.*

Solution. (*i*) $\text{Rate} = -\dfrac{\text{change in partial pressure of } O_2}{\text{time}}$

(minus sign because O_2 is consumed in the reaction).

$$= -\frac{(0.10-0.50)\text{ atm}}{30\text{ min}}$$

$$= \frac{0.40\text{ atm}}{30\text{ min}} = 1.33\text{ atm min.}$$

(*ii*) For an ideal gas, $PV=nRT$ or $P=\dfrac{n}{V}RT=CRT$ or $C=\dfrac{P}{RT}$, thus concentration in moles per litre $\left(\dfrac{n}{V}\right)$ is equal to P (atm) divided by RT

$$\text{Rate} = \frac{1.33\dfrac{\text{atm}}{\text{min}} - \dfrac{1\text{min}}{60\text{ S}}}{0.082\text{ litre atm mol}^{-1}\text{ deg}^{-1}\times 400\text{ deg}}$$

$$= 6.76\times 10^{-4}\text{M s}^{-1}$$

Exercise 6.4. *Consider the reaction* $H_2+I_2 \rightarrow 2HI$ *the rate of disappearance of hydrogen is found to be* 10^{-2} mol L^{-1} s^{-1}. *What would be the corresponding rate of disappearance of iodine and formation of HI? Calculate the rate of this reaction in terms of partial pressure of iodine at 300K assuming that the gases obey ideal gas law.*

Solution. According to the stoichiometry of the equation the various rate expressions are

$$\text{Rate} = -\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

Given,

$$-\frac{\Delta[H_2]}{\Delta t} = 10^{-2}\text{ mol L}^{-1}\text{ s}^{-1}$$

therefore,

$$-\frac{\Delta[I_2]}{\Delta t} = 10^{-2}\text{ mol L}^{-1}\text{ s}^{-1}$$

and $\dfrac{\Delta[HI]}{\Delta t} = 2\times 10^{-2}\text{ mol L}^{-1}\text{ s}^{-1}$

Rate in terms of Pt_2

We know $P=\dfrac{n}{V}RT$ $\left(\text{here } \dfrac{n}{V} = \text{molar concentration}\right)$

Therefore,

$$p_{I_2} = 10^{-2}\text{ mol L}^{-1}\text{ s}^{-1}\times 0.0821\text{ L atm K}^{-1}\text{ mol}^{-1}\times 300\text{ K}$$

$$= 24.6\times 10^{-2}\text{ atm s}^{-1}$$

6.2.5. Instantaneous Rate of Reaction

Calculations involving experimental values of concentrations at different time intervals provide information about average rate of a reaction. Table 6.2 gives concentration of the reactant NO_2 at 10 seconds intervals for the reaction

$$CO(g)+NO_2(g) \rightarrow CO_2(g)+NO(g)$$

TABLE 6.2. Rate data for the reaction $CO(g)+NO_2(g) \rightarrow CO_2(g)+NO(g)$

$t(s)$	$[NO_2]$ mol dm^{-3}	$Rate = -\frac{\Delta[NO_2]}{\Delta t}$ mol dm^{-3} s^{-1}
0	0.100	3.3×10^{-3}
10	0.067	1.7×10^{-3}
20	0.050	1.7×10^{-3}
30	0.040	1.0×10^{-3}
40	0.033	0.7×10^{-3}
100	0.0135	0.3×10^{-3}

The values of rate given in the column 3 are the rate of reaction obtained by dividing the change in concentration of NO_2 in 10 s interval by 10 s. The rates so obtained are also called the average rate of reaction. It can be seen from these rate values given in the column 3 of the Table 6.2, that the rate of the reaction is changing with time. We can obtain a more exact value for the rate

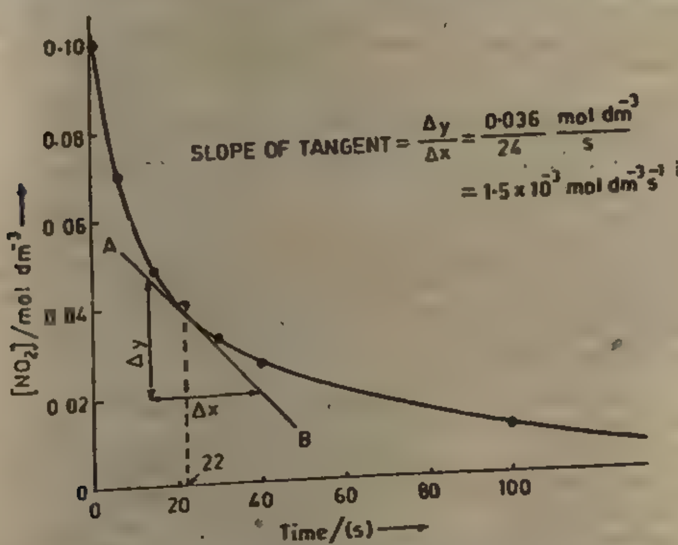


Fig. 6.2. Concentration of NO_2 as a function of time for the reaction

$$CO(g)+NO_2(g) \rightarrow CO_2(g)+NO(g)$$

by reducing the size of time interval. In the limit when Δt approaches zero, $-\left(\frac{\Delta[NO_2]}{\Delta t}\right)$ is the slope of the tangent to the curve at the time t as shown in Fig. 6.2. Thus,

$$\text{Rate}=\text{Limiting value}\left(\frac{-\Delta[NO_2]}{\Delta t}\right)=-\text{Slope of curve}$$

This is the instantaneous rate at a particular time t and the average rate when Δt approaches to zero.

$$r_{ins,\,t}=\lim_{\Delta t\to 0}(r_{av})$$

Thus, for a reaction $A \longrightarrow B$

$$r_{ins,\,t}=-\left(\frac{\Delta[A]}{\Delta t}\right)\lim_{\Delta t\to 0} \quad ...(6.13)$$

Using calculus notations

$$r_{ins,\,t}=-\left(\frac{d[A]}{dt}\right)_t=\left(\frac{d[B]}{dt}\right)_t \quad ...(6.14)$$

Thus the instantaneous rate of a reaction at any particular time during the reaction can be obtained from the slope of the tangent to the concentration versus time curve at that particular moment. The rate of reaction $CO+NO_2 \rightarrow CO_2+NO$ at the time 22 second is determined by drawing a tangent AB at this instance. The slope of the tangent $AB=1.5\times10^{-3}$ mol dm^{-3} s^{-1} is the rate of the above reaction at this moment (Fig. 6.2).

6.3. FACTORS AFFECTING RATE OF A REACTION

The rate of a reaction is affected by the following factors :

1. **Concentration of reactants** : The rate of a reaction increases when the concentration of a reactant is increased. The collision frequency between the molecules that are reacting is first of all dependent on the number of molecules present in a unit volume. As the concentration increases, more reactant molecules collide with one another in a given period of time, resulting in the formation of more molecules of the product.

2. **Temperature of reaction** : A rise in the reaction temperature increases the rate of the reaction. Since the average kinetic energy of the molecules is dependent on the temperature ; in a gas, as the temperature increases, the average kinetic energy increases. This is shown in the Fig. 6.3, which represents the distribution of energy among the molecules in a sample of a gas at two different temperatures. In this figure, temperature T_2 is greater than the temperature T_1. It can be seen that for any particular kinetic energy, such as that indicated by E_a at the temperature T_2, a greater percentage of the molecules have this energy. For example, if E_a represents the

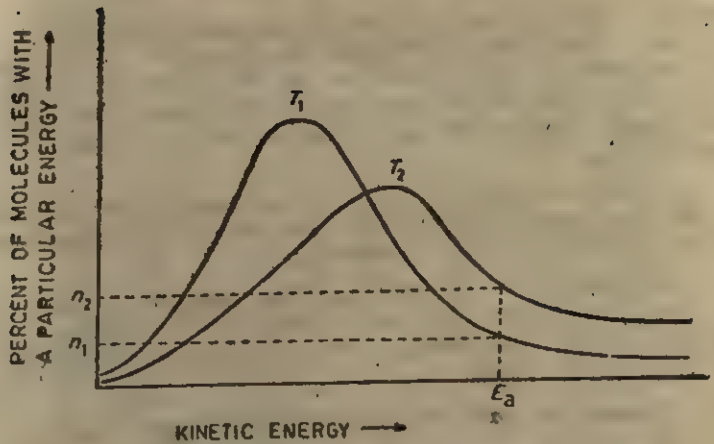


Fig. 6.3. Distribution of energy among molecules at two different temperatures.

activation energy of a particular reaction, there will be more molecules (n_2 versus n_1) having this energy at the temperature T_2 than there are at T_1. Since the molecules have a higher average kinetic energy, more of them have sufficient energy to make their collisions effective, and therefore, the rate of the reaction is higher. As a general approximation, the rate roughly doubles for each 10°C rise in the temperature.

When the temperature of a reaction is changed, the value of the rate constant does change without any change in the rate law.

3. **Catalyst :** A catalyst is a substance that alters the speed of a reaction without being consumed. Generally a catalyst is used to speed up a reaction but there are also catalysts that slow down a

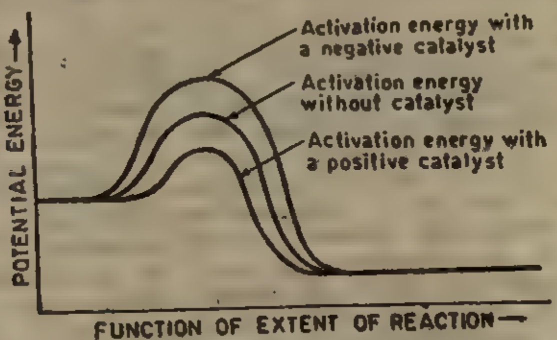


Fig. 6.4. Effect of a catalyst on the activation energy of a reaction.

reaction. A substance of this type is sometimes called a negative catalyst or an inhibiter. A catalyst alters the speed of the reaction by changing the activation energy or the energy barrier. Figure 6.4 shows how a catalyst that speeds up a reaction works by decreasing the activation energy, while a negative catalyst increases the activation energy.

4. **Surface area** : In general, the smaller the size of the reacting particles, the greater is the total surface area for the reaction and consequently the faster is the reaction.

A qualitative and an elementary discussion of all these factors was given in the Unit 11 of Class XI book. We will take up now quantitative aspects of the dependence of reaction rate on the first two factors stated above.

6.3.1. Dependence of Reaction Rate on Concentration

Change in concentration brings a marked change in the rate of a reaction. As the concentration of reactants is increased, the rate of reaction is also increased. The change in the concentration of the reactants of a reaction can be brought about by the following methods :

(*i*) In a gaseous reaction, the concentration of a reactant can be increased by increasing the number of molecules keeping the volume constant or by increasing the pressure over the gas.

(*ii*) In a liquid phase reaction, addition of reactants or removal of solvent will increase the concentration of the reactants.

(*iii*) In a solid phase reaction, addition of reactants or finely dividing the solid will increase the concentration.

(*iv*) In a heterogeneous reaction, the increase in the surface area of solid or liquid phase increases the concentration of reactant in contact.

The actual change in the rate of a reaction as a function of reactant concentration depends on an individual reaction. **There is no method to examine a balanced chemical equation and derive this information from the stoichiometry of the reaction.** Though several attempts were made to obtain a theoretical expression no universal acceptance could be possible. It is important to note that **a mathematical relationship between rate of reaction and reactant concentration can be established only by the experimental study of the reaction under given conditions of concentration.** However,, the rate of a reaction can be related with the concentration of a reactant by raising its power to a simple integer or rational fraction. Thus by doubling the concentration, the rate of a reaction might increase by 2, 2^2, 2^3, $2^{1/2}$, $2^{1/3}$, *etc.* times.

The rate of decomposition of nitrogen pentoxide was observed to be proportional to the concentration of N_2O_5,

$$\text{Rate}=k[N_2O_5]$$

The combination of hydrogen and iodine and photochemical reaction between hydrogen and chlorine can be represented as follows :

$$\text{Rate}=k[H_2]\,[I_2]$$

$$\text{Rate}=k[H_2]^0\,[Cl_2]^0$$

6.4. RATE LAW

The rate law for a chemical reaction is a mathematical expression that relates the rate of the reaction to the concentration of the reactants. It is found experimentally that the rate of a reaction is some function of concentration of the reactant. For a reaction involving a single reactant

$$a\text{A} \longrightarrow \text{products}$$

the rate expression has the general form

$$\text{rate}=k[\text{A}]^p \qquad \text{...(6.15)}$$

For the reaction,

$$a\text{A}+b\text{B} \longrightarrow \text{products}$$

the rate of the overall reaction is proportional to the concentrations of A and B raised to certain powers p and q respectively. This is expressed as

$$\text{Rate of the reaction} \propto [\text{A}]^p[\text{B}]^q$$

or

$$\text{Rate of the reaction}=k[\text{A}]^p[\text{B}]^q \qquad \text{...(6.16)}$$

The concentration of A and B is expressed as mole per cubic decimetre except for gases where pressure units are often used. The values of p and q are whole or fractional numbers or zero. Their values are always determined experimentally.

In the rate law [equations (6·15) or (6.16)], the constant of proportionality, k is known as **rate constant** or **specific reaction rate**. Let the concentration of A and B be 1 mol dm^{-3}. Substituting the unit concentration of A and B in equation (6.16), we have,

$$\text{Rate of the reaction}=k[1]^p[1]^q=k$$

i.e., the rate constant is equal to the rate of the reaction when each reactant has unit concentration. The value of k is independent of the concentrations of the reactants but it is temperature dependent. At a fixed temperature, k is a constant, characteristic of the reaction. For example, for the decomposition of nitrogen pentoxide the value of k at the two different temperatures is given on next page :

Temperature K	Value of k (s^{-1})
308	$1 \cdot 4 \times 10^{-4}$
318	$5 \cdot 0 \times 10^{-4}$

The rate constant is a measure of the intrinsic rate of a reaction, large k values indicate fast reactions and small k indicates slow reactions.

6.5. ORDER AND MOLECULARITY OF REACTION

In the study of chemical kinetics, the reactions are generally classified according to their order or molecularity.

The order of a reaction is defined as "the sum of the powers to which the concentration (or pressure) terms are raised in order to determine the rate of the reaction.

In other words, the sum of the exponents in the rate law is overall order of the reaction. Each exponent gives the order with respect to a certain reactant. The order of a reaction is always experimentally determined. It cannot be predicted theoretically. For example, for the reaction

$$aA \longrightarrow \text{product}$$

if the rate law is,

$$\text{Rate} = k[A]^p$$

then p will be the order of the reaction. Similarly for a reaction,

$$aA + bB + cC \longrightarrow \text{product}$$

where A, B, C are the reactants and a, b, c are the stoichiometric coefficients. Let the experimentally determined rate law for reaction be

$$\text{Rate} = k[A]^p[B]^q[C]^r$$

where k is the rate constant. Here the exponents p, q and r are called the **order of reaction** with respect to A, B and C respectively. The sum $p+q+r$ is known as **overall order** of the reaction. The following points concerning the order of a reaction be carefully noted :

1. **The order of a reaction with respect to different reactants has to be obtained experimentally by determining the rate law.**
2. **The order of reactions are frequently whole numbers but it can also have fractional values, *e.g.*, 0, 1, 2, 3, 3/2, 1/2 *etc*.**
3. **The order of a forward reaction is always positive. However, for a reversible reaction, the order can have negative value also.**
4. **The order of reaction is an experimentally determinable quantity. It cannot be predicted theoretically on the basis of stoichiometry of the reaction.**

5. **A reaction may proceed in several steps, the overall order of the reaction is calculated by the rate determining step.**

Molecularity of a Reaction

It is defined as the number of atoms, ions or molecules taking part in each step leading to the chemical reaction, *i.e.*, the molecularity of a reaction is the number of reactant particles involved in an elementary reaction. For example, the reaction between ozone and nitric oxide,

$$O_3(g)+NO(g) \longrightarrow NO_2(g)+O_2(g)$$

is a bimolecular reaction, an elementary reaction which has two reactant molecules. The reactants in a bimolecular reaction may be the same or different—the point is that two molecules must collide to form the product(s).

Elementary bimolecular reactions

$$A+A \longrightarrow \text{Products}$$
$$B+B \longrightarrow \text{Products}$$

Exercise 6.5. *For the following reactions, rate ations are given. Find the order with respect to each reactant e overall order.*

Reaction	*Rate equation*
(*i*) $3NO(g) \longrightarrow N_2O(g)+NO_2(g)$	Rate$=k[NO]^2$
(*ii*) $H_2O_2+3I^-+2H^+ \longrightarrow 2H_2O+I_3^-(aq)$	Rate$=k[H_2O_2][I^-]$
(*iii*) $CH_3CHO(g) \longrightarrow CH_4(g)+CO(g)$	Rate$=k[CH_3CHO]^{3/2}$
(*iv*) $C_2H_5Cl(g) \longrightarrow C_2H_4(g)+HCl(g)$	Rate$=k[C_2H_5Cl]$
(*v*) $CHCl_3(g)+Cl_2(g) \longrightarrow CCl_4(g)+HCl(g)$	Rate$=k[CHCl_3][Cl_2]^{1/2}$

What are the dimensions of the rate constant in each case ?

Solution. (*i*) Since the rate depends on the second power of NO the order of the reaction with respect to NO and also the overall order is 2.

Dimensions of rate constant

$$\text{Rate}=k[NO]^2$$

or $$\frac{\text{mole}}{(\text{litre})\ (\text{time})}=k\frac{\text{mole}}{(\text{litre})}\ \frac{\text{mole}}{\text{litre}}$$

or $$k=\frac{\text{litre}}{(\text{mole})\ (\text{time})}=\text{L mol}^{-1}\ \text{time}^{-1}$$

(*ii*) Since the rate is dependent on first powers of both H_2O_2 and I^-, the order with respect to each of these is one. As the rate law does not involve the $[H^+]$ concentration term, it can be concluded that the rate of the reaction does not depend on the concentration of H^+ or the power to which $[H^+]$ is raised is zero in the rate law, thus the order of the reaction with respect to H^+ is zero. Thus the overall order of the reaction is $1+1+0=2$. The rate constant dimensions are the same as calculated in (*i*).

k has dimensions : L mol^{-1} $time^{-1}$.

(*iii*) the concentration term is raised to power 3/2 in the rate law. Thus, order of the reaction is 3/2.

k has dimensions,

$$=\frac{\text{rate}}{(\text{concentration})^{3/2}}=\frac{\text{mole (litre)}^{3/2}}{\text{litre (time) (mole)}^{3/2}}$$

$$=L^{1/2}\ mol^{-1/2}\ time^{-1}$$

(*iv*) Since the concentration of C_2H_5Cl has power 1 in the rate law, the order of the reaction with respect to C_2H_5Cl and the overall order is one.

Dimensions for k,

$$k=\frac{\text{rate}}{[C_2H_5Cl]}=\frac{\text{mol}}{\text{(litre) (time)}}\times\frac{\text{litre}}{\text{mol}}$$

$$=time^{-1}$$

(*v*) The rate of the reaction depends on first power of $CHCl_3$ and 0.5 power of Cl_2, the order of the reaction with respect to $CHCl_3$ is one and with respect to Cl_2 is 0.5. The overall order is $1+0.5=1.5$ to determine line dimensions for k. from the rate law k is given by,

$$k=\frac{\text{rate}}{[CHCl_3]\ [Cl_2]^{1/2}}$$

$$=\frac{\text{concentration}}{\text{time (concentration)}^{3/2}}$$

$$=\frac{\text{mol}}{\text{time concentration}^{1/2}}=mol^{-1/2}\ L^{1/2}\ time^{-1}$$

Exercise 6.6. *Rate constants of the following reactions are given below. Convert these rate constants to units as indicated.*

(*i*) $N_2O_5 \longrightarrow 2NO_2+\frac{1}{2}O_2$ *is a first order reaction,* k *is* 1.0×10^{-4} s^{-1}, *change the unit to* min^{-1}.

(*ii*) $2HI \longrightarrow H_2+I_2$ *is a second order reaction. The rate constant* k *is* 1.5×10^{-4} litre mol^{-1} s^{-1}, *change the unit of* k *to* cm^3 mol^{-1} s^{-1}.

Solution. (*i*) In order to find out the rate constant in min^{-1}, the value of k in s^{-1} is to be multiplied by 60 thus $k=1.0\times 10^{-4}$ s^{-1} or $1.0\times10^{-4}\times 60$ min^{-1} or $k=6{\cdot}0\times10^{-3}$ min^{-1}.

(*ii*) To convert litre to cm^3, multiply by 10^3. Thus

$$k = 1.5\times10^{-4}\ \text{litre mol}^{-1}\ \text{s}^{-1}$$
$$= 1.0\times10^{-4}\times10^{3}\ \text{cm}^{3}\ \text{mol}^{-1}\ \text{s}^{-1}$$
$$= 1.0\times10^{-1}\ \text{cm}^{3}\ \text{mol}^{-1}\ \text{s}^{-1}$$

6.6. STUDY OF A REACTION

It has been emphasised that the rate law and order of a reaction can be determined by experiment only. The rate of a reaction is determined by measuring the concentration of a reactant (or product) as a function of time. What we normally do is to choose any property (given in the Table 6.1) which is related to the concentration of one of the species involved in the reaction, and then follow the change in this property as a function of time. Consider the decomposition of nitrogen pentoxide gas,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

A simple method to study this reaction is to measure the pressure of the reaction mixture at different times. From the measured pressure values, it is easy to calculate the partial pressure of N_2O_5 and the concentration of N_2O_5 in moles per decimetre cube. In a typical experiment, the molar concentrations of N_2O_5 at different times is shown in the Table 6.3. These values are plotted in Fig. 6.5. The instantaneous rate of the reaction can be evaluated by drawing tangents at different points of the curve plotted in the Fig. 6.5 and the values of slope which are equal to the rate of reaction are given in Table 6.4. The order of the reaction can now be obtained by Hit and Trial method. Let the rate law for the reaction be

$$\text{rate} = k[N_2O_5]^p$$

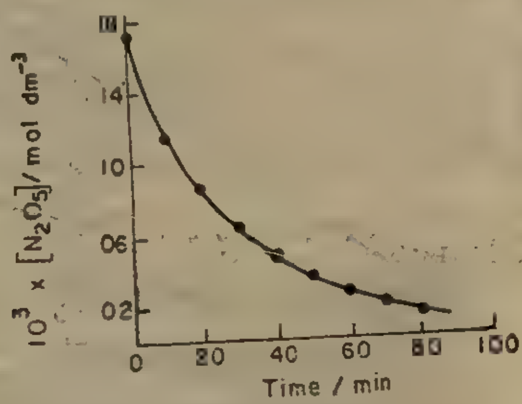


Fig. 6.5. Concentration of N_2O_5 as a function of time.

TABLE 6.3. Concentration-time data for the decomposition of N_2O_5 (g)

Time min	$[N_2O_5]$ mol dm^{-3}
0	1.72×10^{-2}
10	1.13×10^{-2}
20	0.84×10^{-2}
30	0.62×10^{-2}
40	0.46×10^{-2}
50	0.35×10^{-2}
60	0.26×10^{-2}
70	0.19×10^{-2}
80	0.14×10^{-2}

TABLE 6.4. Rate data for decomposition of N_2O_5 (g)

$[N_2O_5]$ mol L^{-3})	*Rate* (mol dm^{-3} min^{-1})
1.72×10^{-2}	
1.13×10^{-2}	34×10^{-5}
0.84×10^{-2}	25×10^{-5}
0.62×10^{-2}	18×10^{-5}
0.46×10^{-2}	13×10^{-5}
0.35×10^{-2}	10×10^{-5}
0.26×10^{-2}	8×10^{-5}
0.19×10^{-2}	6×10^{-5}
0.14×10^{-2}	4×10^{-5}

Taking different values of p, different curves can be plotted between rate of the reaction and the concentration. Two typical curves (taking $p=1$, Fig. 6.6 and $p=2$, Fig. 6.7) showing plots of rate vs $[N_2O_5]$ and rate vs $[N_2O_5]^2$ were obtained.

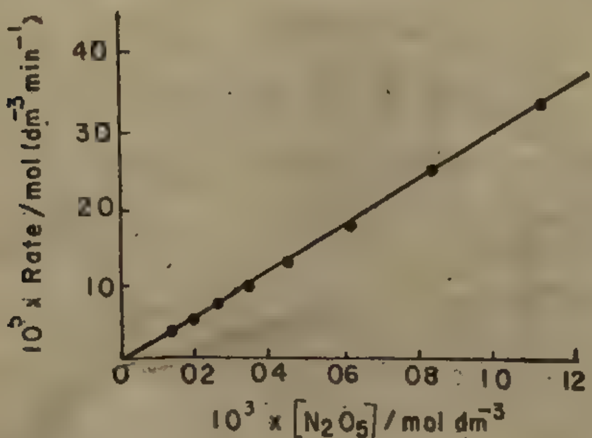


Fig. 6.6. Rate of decomposition of N_2O_5 as a function of $[N_2O_5]$.

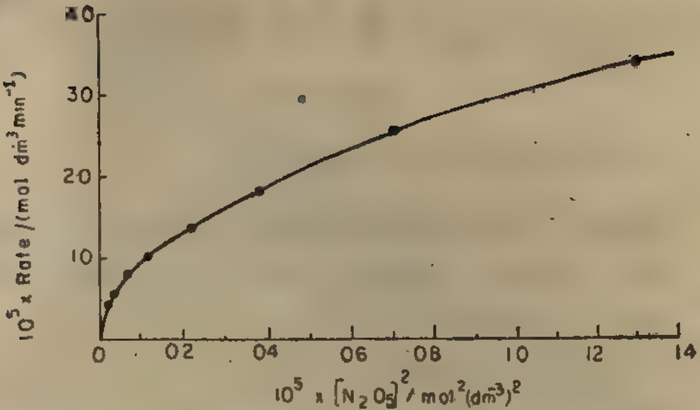


Fig. 6.7. Rate of decomposition of N_2O_5 as a function of $[N_2O_5]^2$.

A straight line obtained in the Fig. 6.6 indicates that decomposition of N_2O_5 is a first order reaction. Thus rate law for the above reaction is,

$$\text{Rate}=k[N_2O_5]$$

Exercise 6.7. *For the following reaction*

$$2A+B+C \longrightarrow A_2B+C$$

the rate law was found to be :

rate=k [A] [B]^2 and the rate constant k is equal to 2.0×10^{-6} mol^{-2} L^2 s^{-1}. *For this reaction*

(*i*) *determine the initial rate when the concentrations of the reactants are as follows :*

$[A]=0.1$ mol L^{-1}

$[B]=0.2$ mol L^{-1} *and*

$[C]=0.8$ mol L^{-1}

(*ii*) *Also determine the rate after 0.44* mol L^{-1} *of A has been reacted.*

Solution. (*i*) As is given the rate law is :

Rate$=k$[A] [B]^2, *i.e.*, the rate of the reaction is independent of the concentration of C. Thus, initial rate is given by

$$\text{Rate}=k[A][B]^2$$

or $=2.0\times 10^{-6}$ mol^{-2} L^2 s$^{-1}\times 0.1$ mol L^{-1} $\times(0.2 \text{ mol L}^{-1})^2$

$=8\times 10^{-9}$ mol L^{-1} s^{-1}.

(*ii*) The reaction is $2A+B+C \longrightarrow A_2B+Cl$ *i.e.*, with 2 moles of A, one mol of B combines. Therefore, with 0.04 mole of A the mole of B which combines

$$=\frac{0.04}{2}=0.02 \text{ mol}$$

The final concentration of $A=0.1-0.04$

$$=0.06 \text{ mol L}^{-1}$$

Similarly, final concentration of $B=0.2-0.02=0.18$ mol L^{-1}.

Substituting concentration of A and B in the rate law, we have

$$\text{Rate}=2\times10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}\times0.06 \text{ mol L}^{-1}\times(0.18 \text{ mol L}^{-1})^2$$
$$=3.9\times10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$$

6.6.1. Method of Initial Rates for Finding Rate Equations

For a reaction which involves more than one reactant, the initial rate method is comparatively an easier way to find the value of rate constant and the order of the reaction. In this method, the initial rate of the reaction is determined as many times as the number of reactants are. Each time while determining the initial rate, the concentration of **only one** of the reactants is changed, while keeping the concentration of all other reactants constant. The experiment is repeated as many times as the number of the reactants, so that the concentration of each reactant is changed while the concentration of all other reactants remains unchanged.

The Exercise 6.8 illustrates this method to determine the order with respect to a reagent and then the overall order of the reaction.

Exercise 6.8. *Three experimental runs were carried out for the reaction between Cl_2 and NO.*

$$Cl_2(g)+2NO(g) \longrightarrow 2NOCl(g)$$

The following rate data were obtained :

Run	*Initial concentrations* $[Cl_2]$	*[NO]* (mol L^{-1})	*Initial rate* (mol L^{-1} s^{-1})
I	0.020	0.010	2.40×10^{-4}
II	0.020	0.030	2.16×10^{-3}
III	0.040	0.030	4.32×10^{-3}

Solution. Let the general form for the rate law be

$$\text{Rate}=k[Cl_2]^p\,[NO]^q$$

The expression for the initial rate, therefore, becomes :

Initial rate $=k[Cl_2]^p_0\,[NO]$

The problem is to determine p, q and k.

We begin by substituting the values from the given data in the general rate expression.

$$(\text{Rate})_{\text{Run I}} = 2.40 \times 10^{-4} = k\,[0.020]^p\,[0.010]^q$$
$$(\text{Rate})_{\text{Run II}} = 2.16 \times 10^{-3} = k\,[0.020]^p\,[0.030]^q$$
$$(\text{Rate})_{\text{Run III}} = 4.32 \times 10^{-3} = k\,[0.040]^p\,[0.030]^q$$

Note that the initial concentration of Cl_2 is constant during Run I and Run II. Similarly, the initial concentration of NO is constant during Run II and Run III. Hence,

$$\frac{(\text{Rate})_{\text{Run II}}}{(\text{Rate})_{\text{Run I}}} = \frac{k\,[0.020]^p \times [0.030]^q}{k\,[0.020]^p \times [0.010]^q}$$

or $$\frac{2.16 \times 10^{-3}}{2.40 \times 10^{-4}} = \left(\frac{0.030}{0.010}\right)^q$$

$$9 = 3^q$$

Therefore, $q=2$, *i.e.* the order with respect to NO is 2.

Similarly,

$$\frac{(\text{Rate})_{\text{Run III}}}{(\text{Rate})_{\text{Run II}}} = \frac{k\,(0.040)^p\,(0.030)^q}{k\,(0.020)^p\,(0.030)^q}$$

$$\frac{4.32 \times 10^{-3}}{2.16 \times 10^{-3}} = \left(\frac{0.040}{0.020}\right)^p$$

$$2 = 2^p$$

Therefore, $p=1$, *i.e.*, the order with respect to Cl_2 is 1,

(*i*) Since the order with respect to NO is 2 and with respect to Cl_2 is 1. The overall order is $2+1=3$.

(*ii*) The rate law for the reaction can now be written by substituting for p and q

$$\text{Rate} = k\,[Cl_2]\,[NO]^2$$

(*iii*) Rearranging we get, $k = \dfrac{\text{rate}}{[Cl_2]\,[NO]^2}$

The value of k can be obtained by substituting in the above expression the data corresponding to any of the runs. For example, taking Run I, we get

$$k = \frac{2.40 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}}{(0.020)\ (\text{mol L}^{-1})\ (0.010)^2\ (\text{mol L}^{-1})^2}$$
$$= 1.20 \times 10^2\ \text{mol}^{-2}.\text{L}^2\ \text{s}^{-1}.$$

6.6.2. Integrated Rate Law Method

So far we have used rate law in the differential form. This rate law can be integrated to a new form of rate law which is more

convenient and precise in telling the rate of reaction. Consider a first order reaction,

$$A \longrightarrow \text{Product}$$

If [A] is the concentration of a reactant A, and k is the rate constant, then for a first-order reaction we have,

$$-\frac{d[A]}{dt}=k[A] \qquad \cdots(6.17)$$

Separating the variables and rearranging the expression,

$$-\frac{d[A]}{A}=k\,dt \qquad \cdots(6.18)$$

Integrating the two sides $-\int \frac{d[A]}{A}=\int k\,dT$, we get

$$-\ln A=k\,t+\text{constant} \qquad \cdots(6.19)$$

where the constant is determined from the initial conditions. For example, let $[A]_0$ be the concentration of A when $t=0$ (*i.e.*, A_0 is the concentration of A at the start of the reaction). Then

$$-\ln [A]=-\ln [A]_0 \text{ when } t=0 \qquad \cdots(6.20)$$

Therefore, the value of the constant is obtained by substituting the value of [A] when $t=0$ in the equation (6.19), we have

$$-\ln [A]_0=0+\text{constant} \qquad \cdots(6.21)$$

Substituting the value of the integration constant in the equation (6.21), we have

$$-\ln A=kt-\ln A_0 \qquad \cdots(6.22)$$

$$\text{or} \quad k=\frac{2.303}{t}\log\frac{[A]_0}{[A]} \qquad \cdots(6.23)$$

$$\text{or} \quad k=\frac{2.303}{t}\log\frac{(\text{initial concentration of the reactant})}{(\text{concentration of the reactant after time, } t)} \qquad \cdots(6.23\,a)$$

6.6.3. Graphic Method for Finding Rate Equations

The general equation for a straight line plot of y vs x is : $y=mx+C$. The integrated rate equation of different order reactions can be arranged in this form. This method is illustrated below for the first order reactions. The rate law (equation 6·23) for the first order reactions is

$$k=\frac{2.303}{t}\log\frac{[A]_0}{[A]} \qquad \cdots(6.23)$$

This equation can be rearranged as

$$\underbrace{\log [A]}_{\text{plot on } y\text{-axis}}=\underbrace{\boxed{\frac{-k}{2{\cdot}303}}}_{\text{slope}}\overbrace{t}^{\text{plot on } x\text{-axis}}+\underbrace{\log [A]_0}_{y \text{ intercept}} \qquad \cdots(6.24)$$

If a plot between log A vs t comes out to be a straight line the reaction will be of the first order with respect to the reactant A. The slope of this line can be used to calculate the rate constant, k. Form the equation (6.24), we know

$$\text{slope} = -\frac{k}{2.303}$$

or $$k = (-2.303)\ (\text{slope of the line}) \qquad \ldots(6.25)$$

Exercise 6.9. *Table 6.5 gives the kinetic data for the decomposition of N_2O_5 at 320K in CCl_4 solution. Calculate (i) the order of the reaction for N_2O_5 decomposition in CCl_4 at 320K by the graphic method.* and *(ii) the value of rate constant, k for the above reaction at this temperature.*

TABLE 6.5. Kinetic data of the decomposition of N_2O_5 in CCl_4 at 320 K

Time/s	*Concentration of N_2O_5 mol L^{-1}*	*Log_{10} [N_2O_5]*
0	2.33	0.3674
185	2.07	0.3160
320	1.90	0.2788
528	1.68	0.2253
1200	1.11	0.0453
1875	0.72	−0.1427
2314	0.55	−0.2596
3140	0.34	−0.4685

Solution. On plotting Log_{10} [N_2O_5] (along y-axis) versus time (along x-axis) a straight line (Fig. 6.8) is obtained. Since the plot between log_{10} [N_2O_5] vs time is a straight line, the reaction—decomposition of N_2O_5 is a first order reaction.

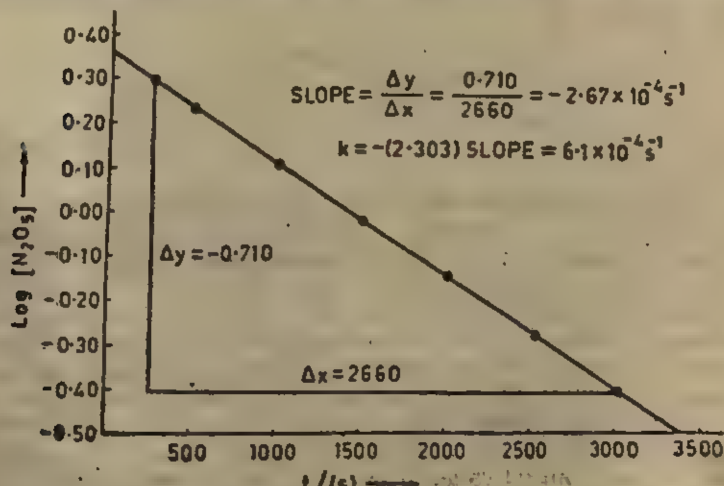


Fig. 6.8. Plot of log_{10} [N_2O_5] versus time

(*ii*) the value of k is obtained from the slope of the line. Here Δx=2660 s and Δy=−0.71

$$\text{slope}=\frac{y}{x}=\frac{-0.710}{2660\ \text{s}}=2.67\times10^{-4}\ \text{s}^{-1}$$

Therefore, $k=-(2.303)\ (\text{slope})$

$$=-2.303\times-2.67\times10^{-4}\ \text{s}^{-1}$$
$$=6{\cdot}1\times10^{-4}\ s^{-1}$$

6.7. HALF-LIFE OF A REACTION

An extremely useful quantity in dealing with reaction rates is the time required for the concentration of a reactant to be reduced to half of its original value—known as the half-life, $t_{1/2}$. Let the initial concentration of the reactant be $[A]_0$ mol dm^{-3}, half-life of this reaction is the time, $t_{1/2}$ when the concentration of reactant becomes $\frac{1}{2}[A]_0$, *i.e.*,

(Concentration of A after half-time)$=\frac{1}{2}[A]_0$

or $\qquad [A]t_{1/2}=\frac{1}{2}[A]_0 \qquad$ (6·26)

Half-life for a first order reaction can be calculated from equation (6.23). The rate law for the first order reactions can be written as

$$t=\frac{2.303}{k}\log\frac{[A]_0}{[A]} \qquad \text{...(6·27)}$$

Substituting the value of [A] from equation (6.26) in the equation (6.27), we have

$$t_{1/2}=\frac{2.303}{k}\log\frac{[A]_0}{\frac{1}{2}[A]_0}=\frac{2.303}{k}\log 2$$

$$t_{1/2}=\frac{0{\cdot}693}{k} \qquad \text{...(6·28)}$$

Equation (6.28) tells us that for a first order reaction, $t_{1/2}$ depends only on k it is constant throughout the reaction). Figure 6·9 gives the half-life, $t_{1/2}$ for the decomposition of N_2O_5 at 330 K—a first order reaction. It can be seen from the Fig. 6.9 that $t_{1/2}$ remains constant, *i.e.*, 7.8 min irrespective of the initial concentration of N_2O_5, *i.e.*, the reactant provided temperature remains constant. It can be seen from the Fig. 6.9 that after each half-time (7·8-min in this case) the concentration of the reactant drops to half of its initial value. During the second half-time the concentration is again cut to half, so after a total of 15·6 min ($2\times t_{1/2}$) the concentration is $\frac{1}{4}$ of its initial value. For a first order reaction the Table 6.6 gives fractions of reactant left after lapse of half-life or its multiple.

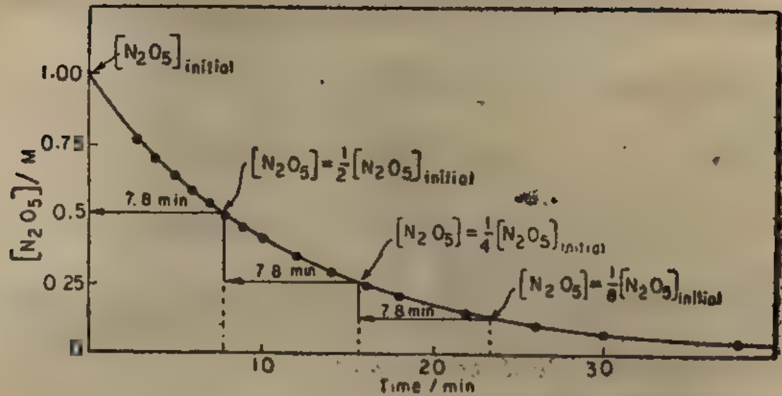


Fig. 6.9. Half-life concept of a reaction : Plot of $[N_2O_5]$ *versus time.*

TABLE 6.6. For a first order reaction

Number of half-life	*Fraction of left out reactant*
0	1
1	1/2
2	1/4
3	1/8
4	1/16
5	1/32
n	$1/2^n$

The rate constant, k varies with temperature, so also $t_{1/2}$ varies with temperature.

Exercise 6.10. *The half-life of the decomposition of dimethyl ether at 720* K *is 26.8* min. *Calculate the rate constant if the reaction is of the first order.*

Solution : $$t_{1/2} = \frac{0.693}{k}$$

or $$k = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{26.8 \text{ (min)}}$$

$$= 2.59 \times 10^{-2} \text{ min}^{-1}$$

Exercise 6.11. *Calculate the half-life of a first order reaction where the specific rate constant is (a) 200* s^{-1} *(b) 10* yr^{-1}.

Solution. $$t_{1/2}=\frac{0.693}{k}$$

(*a*) $$t_{1/2}=\frac{0.693}{200\ (s^{-1})}=3.5\times10^{-3}\ s^{-1}$$

(*b*) $$t_{1/2}=\frac{0.693}{10\ yr^{-1}}=6.93\times10^{-2}\ yr$$

Exercise 6.12. *A reaction which is of the first order with respect to the reactant A has a rate constant 6* min^{-1}. *If we start with the initial concentration of reactant A equal to 0·5* mol L^{-1}, *when would [A] reach the value of 0.05* mol L^{-1} ?

Solution. Rate equation is

$$t=\frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

substituting the values $k=6\ min^{-1}$, $[A]_0=0.5$ mol L^{-1} and $[A]=0.05$ mol L^{-1} in the rate equation we get,

$$t=\frac{2.303}{6\ min^{-1}}\log\frac{(0.5)\ mol\ L^{-1}}{(0.05)\ mol\ L^{-1}}$$

$$=\frac{2.303}{6\ min^{-1}}\log 10$$

$$=\frac{2.303}{6\times min^{-1}}\times1=0.38\ min.$$

Exercise 6.13. *The reaction* $N_2O_5 \longrightarrow 2NO_2+\frac{1}{2}O_2$ *is a first order reaction. Initially the concentration of* N_2O_5 *is 1.0* mol dm^{-3}. *After 3.0* hr *the* N_2O_5 *concentration had decreased to* 1.21×10^{-3} mol dm^{-3}. *What is the half-life of* N_2O_5 *decomposition in minutes ?*

Solution : To calculate the half-life, the rate constant of the reaction should be known. The rate constant for a first order reaction is given by

$$k=\frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

Substituting the values

$$k=\frac{2.303}{3\ hr}\log\frac{1.0\ mol\ dm^{-3}}{1{\cdot}21\times10^{-3}\ mol\ dm^{-3}}$$

$$=\frac{2.303}{3\ hr}\times2{\cdot}9173=2.2395\ hr^{-1}$$

$$t_{1/2}=\frac{0.693}{2.2395}\times60\ min=18.6\ min$$

6.8. DEPENDENCE OF REACTION RATE ON TEMPERATURE

Temperature has a pronounced effect on the rates of chemical reactions. Generally chemical reactions are accelerated by increase in temperature. The oxidation of iron or coal is very slow at ordinary temperatures but proceeds rapidly at high temperatures. In the decolourization of $KMnO_4$ with $C_2O_4^{2-}$ ions, heating is required. The students in the laboratory generally use burner to enhance the rate of reactions. The rates of all the reactions do not change to the same extent for the same temperature change.

We have seen in almost all the reactions that increasing the temperature usually increases the reaction rate. Two questions are generally asked. These are :

1. Why does a temperature rise increase the rate of a reaction ; and
2. Why does a temperature increase have such a large effect ?

To anwer these questions, we return to collision theory. Chemical reactions occur when colliding molecules possess a certain amount of energy called the **activation energy**. Only those collisions which take place between the particles possessing energy equal to the activation energy are effective in bringing out the chemical reaction. We can understand this by considering an analogy of cars bumping each other on a high way. In a line of heavy traffic one frequently receives gentle bumps from the car in front or the car behind. No damage is done to the cars—only to tempers. But occasionally a high speed collision occurs. If this occurs with enough energy, bumper may be knocked off a car and a fender may be dented. It is the high energy collisions which cause damage to the car and it is the high energy molecular collisions which cause the "molecular damage" that we call a chemical reaction. Figure 6.4 gives how the number of molecules possessing a certain energy changes with the change in the temperature.

In 1889 S. Arrhenius gave a mathematical relationship that connects activation energy, E_a, temperature, T, and the rate constant, k. This relationship known as Arrhenius equation is

$$k = A\,e^{-\frac{E_a}{RT}} \qquad \text{...(6.29)}$$

where k=rate constant at T

A=constant

R=gas constant

E_a=activation energy

On taking the log, equation (6.29) becomes :

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad \text{...(6.30)}$$

or $$\log k = -\frac{E_a}{2.303\ RT} + \log A \qquad ...(6.31)$$

It can be seen from the equation (6.31) that reactions which have high values of activation energy have lower values of k and are, therefore, slower.

Equation (6.31) is the equation of a straight line and a plot of $\log k$ (plot on y-axis) versus $\frac{1}{T}$ (along x-axis) should give a straight line with slope equal to $\frac{-E_a}{2.30\ R}$ (Fig. 6.10).

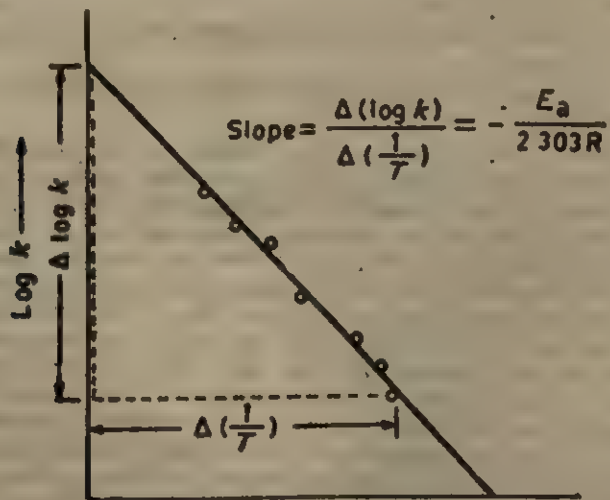


Fig. 6.10. Plot of log k versus $\frac{1}{T}$

The value of the activation energy, E_a, can be found from the slope of a plot of $\log k$ vs $1/T$.

$$E_a = -(\text{slope}) \times 2.303\ T \qquad ...(6.32)$$

6.8.1. Calculation of Activation Energy E_a

If the value of a specific reaction rate, k is known at two different temperatures, the value of activation energy, E_a, can be calculated.

Let k_1 and k_2 be the specific reaction rates at temperatures T_1 and T_2 respectively for the same reaction. Then from the Arrhenius equation, we have

$$\log k_1 = \frac{-E_a}{2.303\ RT_1} + \log A \qquad ...(6.33)$$

and $$\log k_2 = \frac{-E_a}{2.303\ RT_2} + \log A \qquad ...(6.34)$$

Combining the two equations (6.33 and 6.34), we have

$$\log \frac{k_2}{k_1}=\frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right] \quad \text{...(6.35)}$$

Exercise 6·14. *The rate constants of a reaction at two different temperatures are given below :*

Temperature (K)	*Rate constant* ($mol^{-1}\ L\ s^{-1}$)
700	*2.0*
800	*32.0*

Calculate the activation energy for the reaction.

Solution. Substituting the values in the equation (6.35), we have,

$$\log \frac{32}{2}=\frac{E_a}{2.303\times 8.314\ \text{J}}\left(\frac{800-700}{700\times 800}\right)$$

or
$$E_a=\log 16\times \frac{2.303\times 8.314\times 700\times 800}{100}\ \text{J}$$
$$=129.18\ \text{kJ}$$

Exercise 6·15. *The reaction*

$$CH_3N{=}NCH_3\ (g) \xrightarrow{\Delta} N_2\ (g)+2CH_3\ (g)$$

has an activation energy of 2.14×10^5 J mol^{-1} *and at 600* K, *the rate constant is* $1.99\times 10^8\ s^{-1}$. *Does the reaction rate double with 10° ri e in temperature ?*

Solution. Let the rate constant k_1 be at 600 K and k_2 at temperature 610 K. Using the equation (6.35), we have

$$\log \frac{k_2}{k_1}=\frac{E_a}{2.303\ \text{R}}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

or $$\log \frac{k_2}{1.99\times 10^8\ s^{-1}}=\frac{2.14\times 10^{-5}\ \text{J}}{2.303\times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{610\ \text{K}-600\ \text{K}}{600\ \text{K}\times 610\ \text{K}}\right)$$

or $$\log \frac{k_2}{1.99\times 10^8\ s^{-1}}=0.305$$

or $$\log \frac{k_2}{1.99\times 10^8\ s^{-1}}=2.018$$

or $$k_2=2.018\times 1.99\times 10^8\ s^{-1}$$

i.e., the rate for this reaction doubles for 10° rise in the te mperature.

6.9. PHOTOCHEMICAL REACTIONS

We know methane can be chlorinated in the presence of light. Toluene when reacts with chlorine in the presence of UV light forms benzyl chloride ; photographic plate is affected by light ; thus, there are many reactions which are photosensitive. Such reactions are

called photochemical reactions. In such reactions, energy needed by the reacting molecules to overcome the energy barrier is supplied by light. These reactions usually proceed via the formation of free radicals. For example the photochemical combination of hydrogen and chlorine in the presence of light,

$$H_2(g)+Cl_2(g) \xrightarrow{h\nu} 2HCl$$

The reaction is considered to follow the following route :

$$Cl_2+h\nu \longrightarrow 2\,Cl^*$$
$$Cl^*+H_2 \longrightarrow HCl+H^*$$
$$H^*+Cl_2 \longrightarrow HCl+Cl^*$$

Thus, the free radical Cl^* once formed by the absorption of light is regenerated. The chain continues until the reactants are exhausted or Cl^* free radicals combine to give Cl_2.

Reactions which occur with the absorption of light radiations are called photochemical reactions. The light radiations between the range 800 nm and 200 nm wavelength are chiefly used to bring about such reactions. Some of the important observations regarding these reactions are given below :

1. Only those radiations which are absorbed by the reactants are responsible in bringing about a chemical reaction.

2. Sometimes the light absorbed by a substance may be re-emitted as radiations having different wavelengths. This phenomenon is called **phosphorescence**.

3. In some cases molecules which absorb light do not undergo any chemical change, rather they transfer this extra energy to another molecule which may undergo a reaction. This process is called **photosensitisation**. For example, chlorophyll absorbs the sunlight and passes it to carbon dioxide and water in the process—**photosynthesis**.

4. It is always better to use monochromatic radiations.

5. At low intensities of light, the rate of a reaction depends on the intensity of the light.

6. Each reacting molecule in a photochemical reaction absorbs one photon, *i.e.*, one quantum of energy.

6·10. FAST REACTIONS

When you mix sodium chloride and silver nitrate solutions—a white precipitate is formed almost instantaneously. Such reactions where the rate is so high that the time for completion of the reaction cannot be measured with the help of common watches are called fast reactions. Most ionic reactions are fast reactions. Besides ionic reactions, other fast reactions are explosions and combustion reactions. The rate constant of fast reactions is as high as $10^{10}\ s^{-1}$.

It is obvious that the common laboratory techniques, *i.e.*, the measurement of concentration change or pressure developed cannot

be used to study the kinetics of such reactions. To measure the rates of these reactions, devices which can measure very rapid changes in the properties of the reactants or products have to be used. Use of physical methods is the obvious choice since these methods enable to study the change in some property of the reactants/products continuously and the systems have not to be disturbed during the course of the reaction. The device should be such that it establishes a connection between the measured property and the extent of reaction. For example, the reaction between aqueous solution of sodium bicarbonate and hydrochloric acid can be studied by measuring conductance of the solution as a function of time. As the reaction proceeds electrical conductance decreases since HCl is consumed.

Some common techniques generally used to study the fast reactions are :

1. Mass spectrometers
2. Polarography
3. Polarimeter
4. Magnetic resonance
5. Refractometer
6. Spectrophotometer

6.11. MECHANISM OF REACTION

Many reactions take place in two or more steps. The description of various steps (*i.e.*, various elementry reactions) leading to final products is known as reaction mechanism.

In order to ascertain reaction mechanism, first the order of the reaction is determined experimentally. There is usually one slow step, which determines the rate of the reaction and hence, the order of the reaction. Then a guess is made regarding the various other possible steps forming some intermediate compound which quickly decomposes to the products. However, there should be experimental evidence for this assumption. How the study of chemical kinetics helps us to understand the mechanisms of various reactions is illustrated in the following examples.

Exercise 6.16. *A reaction proceeds by the following two steps :*

$$A+B \longrightarrow C$$
$$C+B \longrightarrow D$$

Which is the rate controlling step (slow) if the rate law is

$$rate = k\,[A]\,[B]$$

and what is the overall chemical reaction ?

Solution. $A+B \longrightarrow C$ is the rate controlling

$$A+B \longrightarrow C \text{ (slow)}$$
$$C+B \longrightarrow D \text{ (fast)}$$
$$\overline{A+2B \longrightarrow D \text{ (overall reaction)}}$$

Here C is an intermediate which decomposes almost instantaneously.

Exercise 6.17. *The rate expression for the chemical reaction*

$$NO_2+CO \longrightarrow NO+CO_2$$

is $rate=k[NO_2][CO]$

what is the mechanism for this reaction?

Solution. Reaction seems to take place in a single step, *i.e.*

$$NO_2+CO \longrightarrow NO+CO_2$$

Exercise 6.18. *Given the following mechanism for a reaction,*

$$A+B \longrightarrow D \quad slow$$
$$D+A \longrightarrow E \quad fast$$
$$E+B \longrightarrow C \quad fast$$

write the rate expression and the overall reaction.

Solution. As the slow step determines the rate of the reactio the rate expression would be ;

$$rate=k\,[A]\,[B]$$

The overall reaction is

$$2A+2B \longrightarrow C$$

A few reactions which follow the kinetics of the first order are given below :

1. All radio-active decays
2. Decomposition of NO_2Cl (g)
3. Inversion of cane sugar
4. Hydrolysis of methyl acetate in acid medium
5. The rate of increase in population provided the birth and death rates do not change.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions :

6.1 Choose the correct answer of the four alternatives given for the following questions :

(*i*) Chemical kinetics deals with the measurement of

(*a*) energy changes accompanying the reaction
(*b*) enthalpy change at constant volume
(*c*) rates of reactions
(*d*) equilibrium constants

(*ii*) If the rate of a reaction is independent of the concentration of all reactants, the order of the reaction is

(a) zero (b) one

(c) two (d) three

(iii) If a plot of $\log_{10} C$ versus t gives a straight line for a given reaction, then the reaction is

(a) zero order (b) first order

(c) second order (d) third order

(iv) When concentrations are expressed in mol L^{-1} and time in seconds, the units of the rate constant k, for first order reaction would be

(a) mol L^{-1} s^{-1} (b) L mol^{-1} s^{-1}

(c) s^{-1} (d) L^2 mol^{-2} s^{-1}

(v) The rate of the reaction, A+2B+C→ products, is given by the equation

$$\text{rate}=k[A]^2\,[B].$$

The order of this reaction with respect to C is

(a) zero (b) one

(c) two (d) three

(vi) For a certain reaction it takes 60 seconds for the initial concentration of 0.5 mol L^{-1} to become 0.25 mol L^{-1} and another 60 seconds to become 0.125 mol L^{-1}. What is the order of the reaction ?

(a) zero (b) one

(c) two (d) three

(vii) The half-life of a reaction following the first order kinetics is

(a) independent of initial concentration.

(b) proportional to initial concentration.

(c) inversely proportional to initial concentration.

(d) proportional to square of initial concentration.

(viii) A large increase in the rate of reaction for a rise in temperature is due to the

(a) increase in the number of collisions.

(b) decrease in mean free path.

(c) increase in the number of activated molecules.

(d) increase in the activation energy.

(ix) The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to

(a) 1/2 g (b) 1/4 g

(c) 1/8 g (d) 1/16 g

(x) Consider the reaction

$$3A(g)+B(g)+2C(g) \rightarrow D(g)+2E(g)$$

for which the rate of reaction$=k[A][B]^2$

Doubling the concentration of A increases the rate of the reaction by a factor of :

(a) 2 (b) 3

(c) 4 (d) 8

6.2. Fill in the blanks :

(i) For a reaction, the rate is proportional to [A] and to $[B]^2$, the rate equation would take the form.........

(ii) Rate$=k[A]^2$ indicates a..........order reaction.

(*iii*) Since the quantity $\frac{\text{rate}}{[N_2O_5]}$ is constant, we can write rate$=k$.........; that is, the rate is.........to $[N_2O_5]$.

(*iv*) For any first-order reaction, where A→Products, the rate at any time is.........to [A]. The proportionality constant is known as the ....

(*v*) The Arrhenius equation that connects activation energy, temperature and.........

6.3. **Which of the following statements are true (T) and false (F) ;**

(*i*) For a reaction which takes place in more than one step, the rate determining step is the slow one.

(*ii*) The rate constant for a first order reaction is independent of initial concentration of the reactant.

(*iii*) It is possible to change the value of the specific rate constant for a reaction by changing the temperature.

(*iv*) The rates of most reactions change as the reactions proceed, even if the temperature is kept constant.

(*v*) The half-life of a first-order chemical reaction is independent of temperature.

SHORT ANSWER QUESTIONS

6.4. Rate equations of two reactions are given below. Find out the overall reaction order from the rate equations :

	Reaction	Rate equation
(*i*)	$2NO+H_2 \rightarrow N_2O+H_2O$	Rate$=k\,[NO]^2[H_2]$
(*ii*)	$2NO_2(g)+F_2(g) \rightarrow 2NO_2F(g)$	Rate$=k[NO_2][F_2]$

6.5. Consider the combustion of methane

$$CH_4(g)+2O_2(g) \rightarrow CO_2(g)+2H_2O(g)$$

If methane is burning at a rate of 0.20 mol dm^{-3} s^{-1}, at what rates are CO_2 and H_2O being formed.

6.6. The fungi in the soil removes CO from the earth's atmosphere. What is the apparent order of this process is the rate of CO removal is constant.

6.7. For the chemical reaction A+B→C the following data were obtained,

Experiment	Initial [A] mol L^{-1}	Initial [B] mol L^{-1}	Initial rate mol L^{-1} s^{-1}
I	0.50	0.50	0.02
II	1.00	0.50	0.08
III	1.00	1.00	0.16

Find the rate expression from the above data.

6.8. For a first order reaction having a specific rate constant of 69.3 s^{-1}, calculate the (*i*) half-life, and (*ii*) the time required so that the concentration of 1 mol per litre of the reactant is reduced to 1/16 mole per litre.

6.9 The decomposition of NO_2Cl takes place in the following steps :

$$NO_2Cl \longrightarrow NO_2+Cl \text{ (slow)}$$

$$NO_2Cl+Cl \longrightarrow NO_2+Cl_2 \text{ (fast)}$$

What would be the observed experiment rate law for this reaction ?

6.10. Consider the reaction

$$2ICl+H_2 \longrightarrow I_2+2HCl$$

If the rate constants for this reaction at two different temperatures 230°C and 240°C are found to be 0·163 and 0·348 dm^3 mol^{-1} s^{-1}, respectively. Calculate the value of activation energy.

TERMINAL QUESTIONS

6.1 What is meant by chemical kinetics ? Give a few examples of fast and slow reactions.

6.2 Define rate of a reaction. How does the concentration of reactants affect the rate of a reaction ?

6.3 Derive an expression for rate equation and explain the significance of terms involved.

6.4 Explain the differences between order and molecularity of a reaction.

6.5 List the important factors which affect the rate of a reaction.

6.6 How does temperature affect the rate of a reaction ? How is this effect explained by the concept of energy ?

6.7 Explain why an increase in temperature increases the rate of any reaction indepeadent of whether the reection is endothermic or exothermic.

6.8 Give a suitable example of a first order reaction.

(*a*) Explain the dependence of concentration of the reactant on the (*i*) rate of the reaction, and on the (*ii*) specific reaction rate constant of the reaction.

(*b*) How will you follow the progress of reaction experimentally ?

6·9 Define :

(*i*) initial rate (*ii*) average rate

(*iii*) instantaneous rate (*iv*) rate equation

(*v*) half-life (*vi*) activation energy and

(*vii*) chain reaction.

6.10 Distinguish between rate and rate constant. Give units of rate constant.

6.11 (*i*) What is meant by effective collision.

(*ii*) Only some collisions between molecules are effective in producing chemical reaction. Explain why.

6.12 (*a*) What are photo chemical and fast reactions ?

(*b*) Explain the reaction mechanisms.

6.13 Rate law for the reaction

$$2NO(g)+O_2(g)=2NO_2(g) \text{ is}$$

rate$=k[NO]^2[O_2]$.

How will the rate of the reaction change if the volumes of the reaction vessel is reduced to one-third of its initial value ?

(Ans. Rate will increase 27 times)

6.14 The decomposition of N_2O_5, in carbon tetrachloride solution has been investigated

$$N_2O_5 \text{ (solution)} \rightarrow 2NO_2 \text{ (solution)}+\tfrac{1}{2}O_2(g)$$

The reaction has been found to be of the first order in N_2O_5 with a first order rate constant $6.2\times10^{-4}\ s^{-1}$. Calculate the rate of the reaction when (*i*) $[N_2O_5]=1.25$ mol L^{-1}. What concentration of N_2O_5 would give a rate of 2.4×10^{-3} mol $L^{-1}\ s^{-1}$?

Hint. Rate$=k[N_2O_5]$

[Ans. (*i*) Rate 7.75×10^{-4} mol $L^{-1}\ s^{-1}$

(*ii*) $[N_2O_5]=3.8$ mol L^{-1}

6.15 Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 years. What is the rate constant (in years^{-1}) for the decay ? What fraction would remain after 11540 years ?

(Ans. $t_{1/2}=1{\cdot}2\times10^{-4}$ yr^{-1} ; Fraction remained$=\frac{1}{4}$)

[IIT 1984]

6.16 The experimental data for the position of N_2O_5 in the gaseous phase at 320 K is as follows :

Time/s	$[N_2O_5]$/mol L^{-1}
0	2.00
100	1.88
200	1.77
400	1.56
800	1.21
1200	0.955
1800	0.654
2400	0.450
3000	0.310

(*i*) Plot $[N_2O_5]$ versus time.

(*ii*) From the plot of $[N_2O_5]$ vs time, find the time taken for the concentration of N_2O_5 to change from 10.5 mol L^{-1} to 0.750 mol L^{-1}.

(*iii*) Plot $\log_{10}[N_2O_5]$ vs time

(*iv*) What is the rate law ?

(*v*) Calculate rate constant, *k* from the plot (*iii*).

6.17 The activation energy of the reaction

$$O_3(g)-NO(g) \longrightarrow O_2(g)+NO_2(g)$$

is 10.0 kJ mol^{-1}. How many times will the rate of the reaction change when the temperature is raised from 300K to 310K ?

(Ans. 1.14 times)

ANSWERS TO SELF ASSESSMENT QUESTIONS

6.1. (*i*) *c* (*ii*) *a* (*iii*) *b* (*iv*) *c*
(*v*) *a* (*vi*) *b* (*vii*) *a* (*viii*) *c*
(*ix*) *d* (*x*) *a*

6.2. (*i*) rate$=k[A][B]^2$ (*ii*) second
(*iii*) $[N_2O_5]$, proportional
(*iv*) proportional, specific reaction rate or rate constant.
(*v*) rate constant,

or $k=Ae^{-\frac{Ea}{RT}}$

6.3. (*i*) T (*ii*) F (*iii*) T (*iv*) T (*v*) F

6.4. (*i*) Examining the rate equation shows that in the rate law, the concentration of NO is raised by power 2 and the concentration of H_2 is raised by the power 1, the reaction is of, 2+1=3, *i.e.*, third order.

(*ii*) In the rate law, the sum of the powers to which concentration terms are raised is 1+1=2, *i.e.*, the reaction is of second order.

6.5. $$\text{Rate}=-\frac{\Delta(CH_4)}{\Delta t}=\frac{\Delta[CO_2]}{\Delta t}=\frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}.$$

The rate at which CO_2 is formed is given by

$$\frac{\Delta[CO_2]}{\Delta t}=0.20 \text{ mol dm}^{-3}\text{ s}^{-1}$$

The rate of formation of water can be written as

$$\frac{\Delta[H_2O]}{\Delta t}, \text{ since } \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}=\text{rate}=0.20 \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$\frac{\Delta[H_2O]}{\Delta t}=2\times 0{\cdot}20=0.40 \text{ mol dm}^{-3}\text{ s}^{-1}$$

6.6. Since the rate does not depend upon the concentration of CO, it has zero order.

6.7. Let rate law be, rate$=k[A]^p[B]^q$ From experiment II divided by experiment I gives,

$$\frac{k[1.0]^p[0.5]^q}{k[0.5]^p[0.5]^q}=\frac{0.08}{0.02}$$

or $(2)^p=4$

or $p=2$.

Similarly $\frac{\text{expt. III}}{\text{expt. II}}$ gives

$$\frac{k[1.0]^p[1.0]^q}{k[1.0]^p[0.5]^q}=\frac{0.16}{0.08}$$

or $(2)^q=2$

or $q=1$

Substituting the values of p and q the required rate law is,

$$\text{rate}=k[A]^2[B]$$

6.8. (*i*) $t_{1/2}=\frac{0.693}{k}=\frac{0.693}{69.3\ s^{-1}}=10^{-2}$ s

(*i*) We know

$$t=\frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

Here $k=69.3\ s^{-1}$, $[A]_0=1.0$ mol L^{-1}

$$[A]=\frac{1}{16}\text{ mol }L^{-1}$$

Substituting the values

$$t=\frac{2.303}{69.3\ s^{-1}}\log\frac{1\text{ mol }L^{-1}}{1/16\text{ mol }L^{-1}}$$

$$=\frac{0.303}{69.3s^{-1}}\times1.2041=4\times10^{-2}\text{ s}$$

6.9. Since the first step is the slow step, it is the rate determining step. Thus the rate law for the overall reaction should be the same as the rate law for the rate-determining step. Since only one molecule of NO_2Cl is involved. The rate law would be

$$\text{rate}=k[NO_2Cl]$$

6.10. We know from Arrhenius equation

$$\log\frac{k_2}{k_1}=\frac{Ea}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

Substituting the values

$$\log\frac{0.348\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}}{0.163\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}}=\frac{Ea\,[513K-503K]}{2.303\times8.314\times10^{-3}\text{ kJ mol}^{-1}\text{ K}^{-1}\ 513K\times503K}$$

mol^{-1} K^{-1} 513K × 503K

$$\text{or}\quad Ea=\log\frac{2{\cdot}134\times(2.303\times8.314\times10^{-3}\times513\times503)}{10}\text{ kJ mol}^{-1}$$

$$=162{\cdot}6\text{ kJ mol}^{-1}$$

□□

UNIT 7

Organic Chemistry Based on Functional Group-I

(Haloalkanes, Haloarenes, Alcohols and Phenols)

Science is a tree of many branches, bountiful are its fruits to man in more complete healthful living.

UNIT PREVIEW

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Describe and give examples of the group of organic compounds called haloalkanes, haloarenes, alcohols and phenols.
2. Give the definition of structural isomerism and recognize structural isomers.
3. Deduce the IUPAC names of the organic compounds given the structural formulae and vice versa.
4. Recognize and name an alkyl halide, an aryl halide, an alcohol and a phenol from the formulae.
5. Give the methods of preparation of the compounds included in the unit.
6. Correlate the variation observed in physical properties of these compounds with their structures.

7. Describe the chemical reactions of the compounds included in the unit.
8. Understand the terms : nucleophilic and electrophilic substitution.
9. Give the name reactions.
10. Describe the chemistry of some important polyhalogen and polyhydroxy compounds.

PART I

HALOALKANES AND HALOARENES

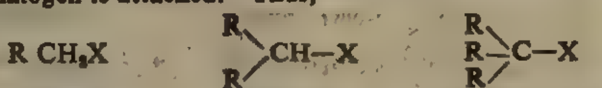
7.1. INTRODUCTION

We have studied in Class XI about the outstanding property of carbon to form a vast number of covalent compounds. Organic compounds that contain only carbon and hydrogen atoms are called **hydrocarbons**—alkanes, alkenes, alkynes and arenes. Hydrocarbons are the parent compounds for the formation of a variety of carbon compounds. Halogenation of alkanes produces organic compounds called **haloalkanes**. These covalent compounds are also known as **alkyl halides**. The general formula for haloalkanes is RX, where R is an alkyl (C_nH_{2n+1}) group and X represents a halogen atom. As the name of the series implies, the compounds are derived from the substitution of a hydrogen atom in an alkane by a halogen.

Haloarenes are aromatic compounds in which the halogen atom is attached directly to the carbon atom of the aromatic ring (C_6H_5—X). These compounds are also derived from the replacement of a hydrogen atom in arenes by a halogen atom. Haloarenes are also known as **aryl halides**.

The chemical reactivity of these compounds is centred on the halogen atom, which is the functional group. Alkyl fluorides differ markedly from chloro-, bromo- and -iodo-alkanes, which are very similar in character. The variations in their chemistry arise from variations in the carbon skeleton. Haloalkanes and haloarenes are particularly valuable in organic synthesis because the halide ion can be readily displaced by a nucleophile.

Alkyl halides are further classified into primary, secondary and tertiary compounds depending upon the nature of carbon to which halogen is attached. Thus,



Primary alkyl halide — Secondary alkyl halide — Tertiary alkyl halide

Alkylhalides are classified as mono-, di-, tri-, and tetra-halogen compounds derivatives depending upon the number of the halogen atoms present in the molecule :

CH_3Cl, Methyl chloride or chloromethane

CH_2Cl_2, Methylene chloride or dichloremethane

$CHCl_3$, Chloroform or trichloromethane

CCl_4, Carbon tetrachloride or tetrachloromethane

7.2. NOMENCLATURE

The common alkyl halides are better known by their trivial names, *viz.*, the halide of the corresponding alkyl group. In the IUPAC system, the halogen is regarded as a substituent on the parent hydrocarbon chain. The trivial and the IUPAC names of some common alkyl chlorides are given in Table 7.1. Alkyl halides are named as monohalogen substituted alkanes.

Among aryl halides, chlorobenzene may be considered as a typical example and is referred to as nuclear substituted. When the halogen is present in the side-chain (*e.g.*, in benzyl chloride) it behaves like alkyl halides, rather than aryl halides,

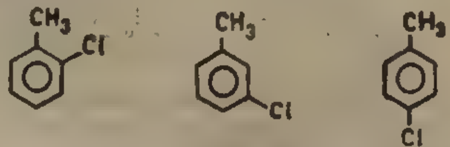
Chlorobenzene Benzyl chloride

TABLE 7.1. Common and IUPAC names of some alkyl halides

Formula	*Trivial (common) name*	*IUPAC name*
CH_3Cl	Methyl chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2Cl$	*n*-Propyl chloride	1-Chloropropane
$(\overset{1}{H_3C})(\overset{3}{H_3C})\overset{2}{C}H-Cl$	iso-propyl chloride	2-Chloropropane
$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-Br$	*n*-Butyl bromide	1-Bromobutane
$\overset{1}{C}H_3-\overset{2}{C}H(Cl)-\overset{3}{C}H_2-\overset{4}{C}H_3$	sec-Butyl chloride	2-Chlorobutane
$(\overset{3}{H_3C})(H_3C)\overset{2}{C}H-\overset{1}{C}H_2Br$	iso-butyl bromide	1-Bromo 2-methyl propane
$(\overset{1}{H_3C})(H_3C)(\overset{3}{C}H_3)\overset{2}{C}-Cl$	tert-Butyl chloride	2-Chloro-2-methyl propane

In naming haloarenes, the prefixes, choro-, bromo-, *etc.*, are added before the name of the hydrocarbon. In a benzene ring, the relative positions of substituents at 1, 2- ; 1, 3- ; and 1, 4- positions are shown by the prefixes ortho (*o*-), meta (*m*-) and para (*p*-) respectively.

Accordingly there are three isomers of disubstituted benzenes, *e.g.*, for chlorotoluene,



o-Chlorotoluene (2-Chlorotoluene)   m-Chlorotoluene (3-Chlorotoluene)   p-Chlorotoluene (4-Chlorotoluene)

7.3. HALOALKANES AND HALOARENES

In this section, we shall study about some of the methods of preparation and the properties of haloalkanes and haloarenes.

Alkyl and aryl halides are synthetic products, *i.e.*, do not occur in nature. Alkyl halides are conveniently prepared either from alcohols and alkanes by substitution or alkenes by addition reactions.

7.3.1. Preparation of Alkyl Halides

1. Alkyl halides from hydrocarbons

(*i*) **Halogenation of alkanes** : Direct halogenation of alkanes in the presence of heat, light and a catalyst gives alkyl halides.

$$\underset{\text{Alkane}}{R{-}H} + X_2 \longrightarrow \underset{\text{Alkyl halide}}{R{-}X} + HX$$

Reaction with chlorine is faster than bromine. The reaction with iodine is reversible. This method yields mixtures of mono and poly substituted products.

Though it is difficult to separate these mixtures, the mixtures themselves are sometimes useful as industrial solvents.

(*ii*) **Addition of halogen acids to alkenes** : Alkyl halides are also prepared by the addition of halogen acids (HX) to an alkene.

$$\underset{\text{Alkene}}{RCH{=}CH + HX} \longrightarrow \underset{\text{sec-Alkyl halide}}{RCHXCH_3}$$

Addition of halogen acids to alkenes is governed by Markovnikov's (or Markownikoff's) Rule. According to Markovnikov the negative part of the molecule adding to the double bond goes to that

carbon atom which is linked to the least number of hydrogen atoms. However, in the presence of peroxides such as benzoyl peroxide, $C_6H_5-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5$, the addition of HBr to unsymmetrical olefins takes place contrary to the Markovnikov's rule. This is known as **peroxide effect** or **Kharsch effect**.

$$CH_3CH{=}CH_2 + HBr \xrightarrow{\text{with peroxide}} \underset{\substack{n\text{-Propyl bromide} \\ \text{(1 Bromo propane)}}}{CH_3CH_2CH_2Br}$$

Propene

$$CH_3CH{=}CH_2 + HBr \xrightarrow[\text{peroxide}]{\text{without}} \underset{\text{Isopropyl bromide}}{CH_3CHBrCH_3}$$

2. Alkyl halides from alcohols

$$R{-}OH \longrightarrow R{-}X$$

This is the most important method for the preparation of alkyl halides. A number of halogen reagents are available and the choice is usually based on the availability of reagents.

(*i*) **Reaction with hydrogen halides and concentrated hydrohalic acids** : These react with alcohols in the presence of dehydrating agents like anhydrous $ZnCl_2$ and H_2SO_4 which prevent the reverse reaction with water to alcohol (see industrial preparations below). The reactivity of alcohols decreases in the order : tertiary> secondary>primary.

For preparing the bromides and iodides, hydrogen bromide and iodide are usually prepared in situ (*e.g.*, using NaBr/conc. H_2SO_4 and KI/H_3PO_4 respectively).

$$CH_3{-}CH_2{-}OH + HCl \xrightarrow{ZnCl_2} CH_3{-}CH_2{-}Cl + H_2O$$

$$CH_3{-}CH_2{-}OH + NaBr + H_2SO_4 \longrightarrow CH_3{-}CH_2{-}Br + H_2O + NaHSO_4$$

(*ii*) **Reaction with phosphorus halides or thionyl chloride** : Thionyl chloride is preferred as the by-products are gases which makes the purification of the alkyl halide easy.

$$\underset{\text{Alcohol}}{ROH} + PCl_5 \longrightarrow \underset{\text{Alkyl chloride}}{RCl} + POCl_3 + HCl$$

$$\underset{\text{2-Propanol}}{CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_3} + PCl_5 \longrightarrow \underset{\text{2-Chloropropane}}{CH_3{-}\underset{\underset{Cl}{|}}{CH}{-}CH_3} + POCl_3 + HCl$$

$$\underset{\text{Methyl alcohol}}{3CH_3OH} + PCl_3 \longrightarrow \underset{\text{Methyl chloride}}{3CH_3Cl} + H_3PO_3$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + SOCl_2 \longrightarrow \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + SO_2 + HCl$$

Alkyl iodides and bromides are prepared using a mixture of red phosphorus and iodine or bromine.

$$2P + 3Br_2 \longrightarrow 2PBr_3$$

$$\underset{\text{Alcohol}}{3R\,OH} + PBr_3 \longrightarrow \underset{\text{Alkyl bromide}}{3R\,Br} + H_3PO_3$$

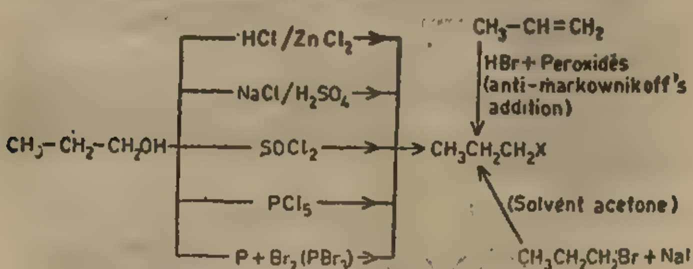
$$\underset{\text{Propanol}}{CH_3CH_2CH_2OH} \xrightarrow{PI_3} \underset{\text{Propyl iodide}}{CH_3CH_2CH_2I} + H_3PO_3$$

3. From other alkyl halides

Alkyl iodides may be conveniently prepared from the corresponding chlorides or bromides by the action of sodium iodide dissolved in acetone. NaBr and NaCl are insoluble in acetone and precipitate out, thus driving the reaction to the right.

$$CH_3{-}CH_2{-}Cl + NaI \xrightarrow{\text{Acetone}} CH_3{-}CH_2{-}I + NaCl$$

The various methods of preparation are summarized below :



X=Cl/Br/I depending on the reagent.

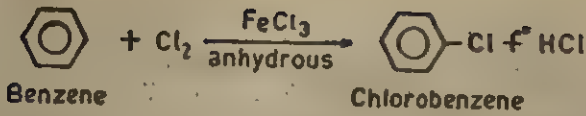
Some of the important preparative methods with their details are portrayed in Fig. 7.1.

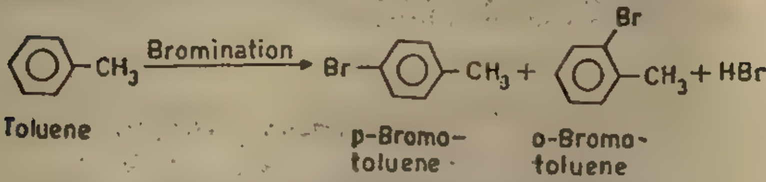
7·3·2. Preparation of Haloarenes

Though alcohols are the usual starting materials for the preparation of alkyl halides, aryl halides are not generally prepared from phenols as it is not easy to replace the hydroxyl group of phenols by any other group.

1. Halogenation of aromatic hydrocarbons

The usual method is direct halogenation of aromatic hydrocarbons in the presence of a 'halogen carrier' like iron chloride (Lewis acid). Metallic iron and AlX_3 can also be used.





In this reaction, catalyst produces an electrophile (electron deficient species) from the attacking halogen molecule,

$$Cl_2 + FeCl_3 \longrightarrow Cl^{\delta+} \cdots [Cl \cdots FeCl_3]^{\delta-}$$

which attacks the aromatic hydrocarbon. This method is suitable for the preparation of chloro- and bromoarenes only. With iodine, the reaction is reversible. But if the reaction is carried out in the presence of oxidizing agents like HIO_3 or HNO_3, an iodoarene compound will be obtained.

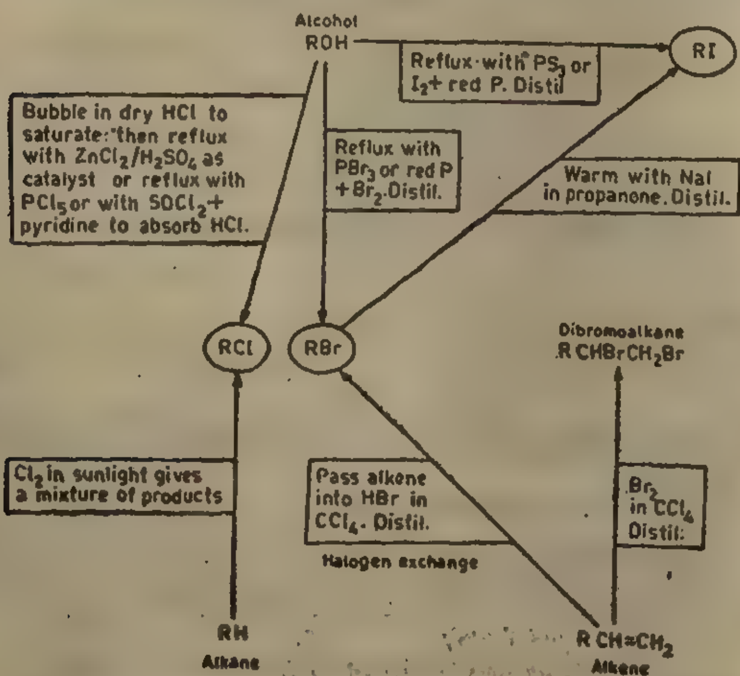
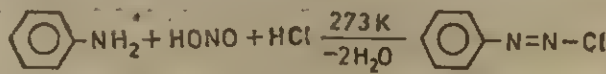


Fig. 7.1. Laboratory methods used for the preparation of halogenoalkanes.

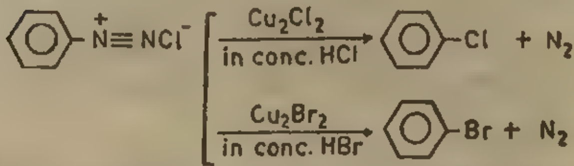
2. From diazonium salts

This method involves the warming of an aqueous solution of a diazonium salt with cuprous halide and hydrohalic acid (Cu_2Cl_2 and HCl or Cu_2Br_2 and HBr). The diazo group (—N=N—) of salt is replaced by a halogen atom forming a corresponding halide. This reaction is known as **Sandmeyer's reaction.** The diazonium salt is obtained by treating an amino compound with ice cold nitrous acid ($NaNO_2$+HCl) at low temperatures. The salt is highly reactive.

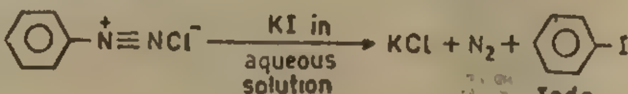


Aniline

Benzene diazonium chloride



Alkyl iodides are obtained by treating the diazonium salt with potassium iodide.



Iodo-benzene

Fluoroarenes are obtained by decomposing the corresponding diazonium tetrafluoroborate

Benzene diazonium tetrafluoroborate

7.3.3. Physical Properties

Since the alkyl halides have higher molecular masses than the corresponding alkanes, they melt and boil at higher temperatures. The lower alkyl halides are gases at room temperature while higher one are liquids.

For a given alkyl group, the boiling points of the halides follow the order (Fig 7·2, Table 5.1)

$$RF < RCl < RBr < RI$$

The atomic mass of the halogens, and the polarity of C—X bond tend to make boiling points fairly high for a given size of carbon chain.

TABLE 15.1. Boiling points of some alkyl halides

Alkyl radical	*Fluoride* bpK	*Chloride* bpK	*Bromide* bpK	*Iodide* bpK
Methyl	194.4	248.8	276.6	315.5
Ethyl	235.5	285.0	311.0	345.0
Propyl	269.8	320.2	343.9	375.4
n-Butyl	305.0	351·0	374.6	404.0
sec-Butyl	—	341.0	364.0	392.0
tert-Butyl	—	324.0	346.0	373.0

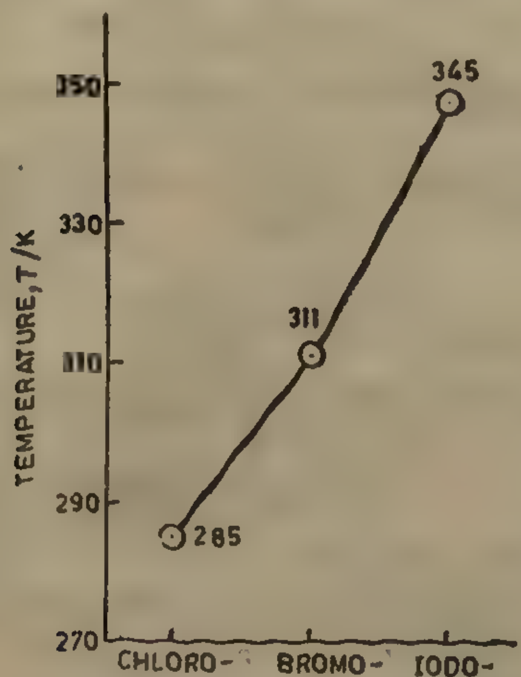


Fig. 7 2. Boiling points of ethylhalides.

The primary halides generally have the highest boiling points within a given group of isomers.

Though polar in nature, the alkyl halides are normal liquids and not associated like alcohols. Organic halides are insoluble in water because of their inability to form H-bonds with water or to break the H-bonds already present in water. However they are soluble in common organic solvents (like dissolves like). Alkyl halides are colourless when pure and have a pleasant odour. Alkyl chlorides are usually lighter than water while alkyl bromides and iodides are usually heavier than water. Their densities follow the order : $RF < RCl < RBr < RI$. Aryl halides are relatively high melting solids or high boiling liquids and immiscible with water. They are also soluble in organic solvents.

In disubstituted compounds (*e.g.*, dichlorobenzenes), the para-isomer has a much higher mp than either the ortho- or meta-isomer (Fig. 7.3). This is because *p*-dichlorobenzene is symmetrical and can fit better in the crystal lattice of the solid, *i.e.*, they have a higher intracrystalline forces. Again, for this reason the *p*-isomers are usually less soluble in a given solvent than the '*o*'-isomers.

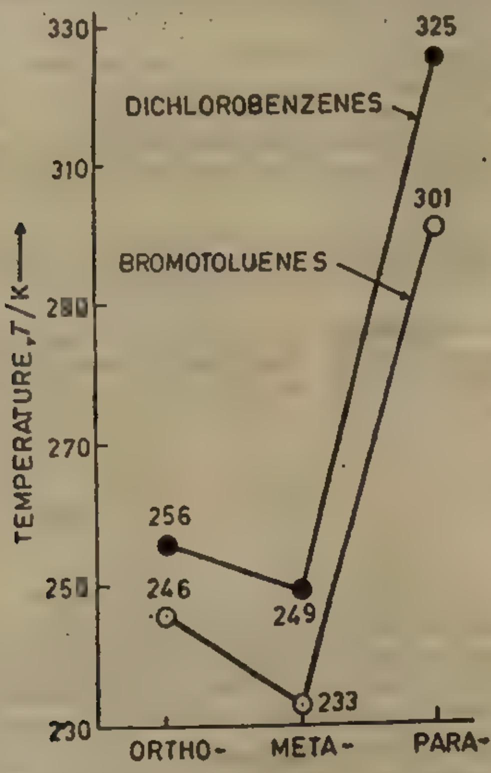


Fig. 7.3. Melting points of dichlorobenzenes and bromotoluenes.

7.3.4. Chemical Properties

Alkyl halides are versatile intermediates for the preparation of a variety of organic compounds. Aryl halides (with halogens on sp^2 hybridized carbons) are much less reactive and undergo substitution only under rather drastic conditions.

Alkyl and aryl halides have significant dipole moments which indicate that the carbon-halogen bond is partially polarized. This

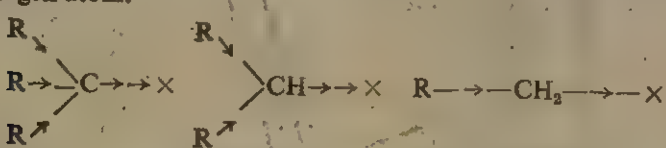
$$-\overset{|}{\underset{|}{\overset{\delta+}{C}}}-\overset{\delta-}{X} \rightarrow -\overset{|}{\underset{|}{C}}\,\delta+ \quad \overset{\delta-}{:X}$$

is due to the higher electronegativity of halogen than carbon. This is referred to as the inductive effect. The dipole moments of alkyl halides range from 2.05 to 2.15 D. The dipole moment of chlorobenzene is 1.73 D

Thus, the reactivity of alkyl halides depends upon (*i*) the nature of the halogen atom, and (*ii*) the nature of the alkyl group. For a given alkyl group the order of reactivity is iodide>bromide >chloride, *i.e.*, $C_2H_5I > C_2H_5Br > C_2H_5Cl$. For a given halogen, the order of reactivity is tertiary>secondary>primary alkyl group, *i.e.*,

$$R_3C-Cl > R_2CH-Cl > R-CH_2-Cl$$

This can be explained on the basis that alkyl group is electron repelling (exerts +I effect). The larger the number of alkyl groups attached to a carbon atom the greater will be the reactivity of halogen atom.

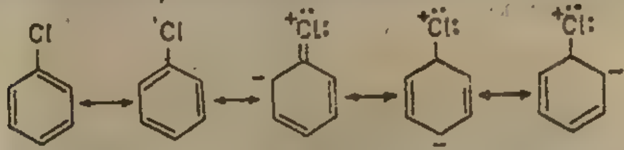


Tertiary Secondary Primary

Alkyl halides, due to the partial positive charge on the carbon atom, undergo nucleophilic substitution reactions. Reagents involved in such reactions are called nucleophilic reagents (from the Greek nucleophilic-nucleus loving) and are rich in electrons.

Aryl halides are reluctant to undergo these nucleophilic substitution reactions and are normally inert to water, aqueous alkali, ammonia, potassium cyanide, and so on. This is attributed to the development of double bond character between halogen and carbon

through resonance. This effect is described in terms of the delocalization of a lone pair of electrons from halogen,



(I) (II) (III) (IV) (V)

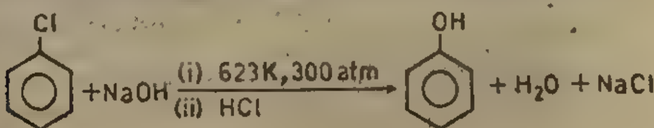
(*i*) **Halogen substitution (replacement) reactions :** This is the most important type of reaction which is initiated by electron rich reagents (nucleophiles) attacking the alkyl halides,

$$\underset{\text{Substrate}}{-\overset{|}{\underset{|}{C}}\overset{\delta+\quad\delta-}{-\!\!-\!\!-}X} \quad + \underset{\text{Nucleophile}}{Nu:} \longrightarrow \underset{\text{Product}}{-\overset{|}{\underset{|}{C}}-\!\!-\!\!-Nu} + \underset{\text{Leaving group}}{X}$$

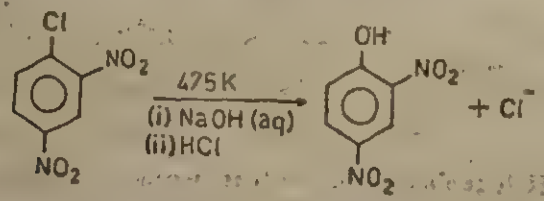
A wide variety of compounds may be prepared using different nucleophiles.

Reagent (RX —)	Products	Class
$\xrightarrow{OH^-}$	$X^- + R{-}OH$	Alcohols
$\xrightarrow{OR'}$	$X^- + R{-}OR'$	Ethers
$\xrightarrow{NH_3}$	$X^- + R{-}NH_2$	Primary amines
$\xrightarrow{NH_2R'}$	$X^- + R{-}NHR'$	Secondary amines
$\xrightarrow{NHR_2'}$	$X^- + RNR'_2$	Tertiary amines
$\xrightarrow{CN^-}$	$X^- + R{-}CN$	Alkyl cyanide
$\xrightarrow{AgCN}$	$AgX + R{-}N{\equiv}C$	Alkyl isocyanide
$\xrightarrow{NO_2^-}$	$X^- + R{-}NO_2$	Nitroalkane
$\xrightarrow{AgNO_2}$	$X^- + R{-}O{-}NO$	Alkyl nitrite
$\xrightarrow{SR^-}$	$X^- + R{-}S{-}R'$	Thioether
$\xrightarrow{I^-}$	$X^- + RI$	Alkyl iodide

Nucleophilic substitution of aryl halides can be carried out only under drastic conditions, *e g*., chlorobenzene is converted to phenol by NaOH only under high temperature and pressure.



If $-NO_2$ or $-SO_3H$ (*i.e.*, strong electron withdrawing groups) are present in *o*- or *p*-positions, then replacement of halogen is fairly easy. This is sometimes referred to as 'activated nucleophilic aromatic substitution'.



This important effect of the nitro group on aromatic halogen compounds depends upon the ability of the nitro groups to delocalize negative charge.

(*ii*) **Elimination reactions**

When a halogenalkane is treated with an alcoholic solution of potassium hydroxide, the elimination of hydrogen halide occurs to give an alkene. This reaction, at times, is called **dehydrohalogenation reaction.**

$$-\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-\overset{\displaystyle X}{\underset{|}{\overset{|}{C}}}- \xrightarrow[\text{Elimination}]{KOH/C_2H_5OH} \rangle C=C\langle + KX + H_2O$$

This elimination reaction is often useful for alkene synthesis, although for ethylene itself the reaction is ineffective and is generally poor when primary alkyl halides are used.

$$CH_3-CH_2-CH_2Br \xrightarrow{KOH/C_2H_5OH} \underset{\text{Propylene}}{CH_3-CH_2-CH=CH_2} + KBr + H_2O$$

(*iii*) **Reaction with metals**

When alkyl and aryl halides are refluxed in dry diethyl ether with magnesium, the metal slowly dissolves with the formation of R–MgX, called **Grignard reagent.**

$$\underset{\text{Alkyl halide}}{RX} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R-Mg-X}$$

For example : $CH_3Br + Mg \xrightarrow{\text{Dry ether}} CH_3MgBr$
Methyl magnesium bromide (Grignard reagent)

$$C_6H_5Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Phenyl magnesium bromide}}{C_6H_5MgBr}$$

Grignard reagents are versatile substances by the use of which varied types of organic compounds can be synthesized. Thus the reaction of methyl magnesium bromide with a carbonyl compound proceeds as follows :

$$\begin{matrix}R\\R'\end{matrix}\!\!>C=O+Mg\!\!<\!\!\begin{matrix}CH_3\\Br\end{matrix}\longrightarrow\begin{matrix}R\\R'\end{matrix}\!\!>C\!\!<\!\!\begin{matrix}OMgBr\\CH_3\end{matrix}\xrightarrow{HOH}\underset{\text{tert-Alcohol}}{\begin{matrix}R\\R'\end{matrix}\!\!>C\!\!<\!\!\begin{matrix}OH\\CH_3\end{matrix}}$$

This reaction is quite useful for the synthesis of alcohols, as will be seen later in this unit.

$$RMgX\begin{cases}\xrightarrow{HOH} RH & \text{Hydrocarbon}\\ \xrightarrow[(ii)\ H^+]{(i)\ CO_2} RCO_2H & \text{Carboxylic acid}\\ \xrightarrow{HCHO} RCH_2{-}OH & \text{Primary alcohol}\\ \xrightarrow{R'CHO} R{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}R' & \text{Secondary alcohol}\\ \xrightarrow{R'COR''} R{-}\overset{\displaystyle R'}{\overset{|}{\underset{\displaystyle R''}{\underset{|}{C}}}}{-}OH & \text{Tertiary alcohol}\end{cases}$$

Some reactions of Grignard reagents.

Both alkyl and aryl halides react with lithium forming alkyl lithium.

$$RX+2Li\xrightarrow{\text{Dry ether}}RLi+LiX$$

For example,

$$\underset{\text{Butyl bromide}}{C_4H_9Br+2Li}\xrightarrow{\text{Dry ether}}\underset{\text{Butyl lithium}}{C_4H_9Li}+LiBr$$

$$\underset{\text{Bromtbenzene}}{C_6H_5Br+2Li}\xrightarrow{\text{Dry ether}}\underset{\text{Phenyl lithium}}{C_6H_5Li}+LiBr$$

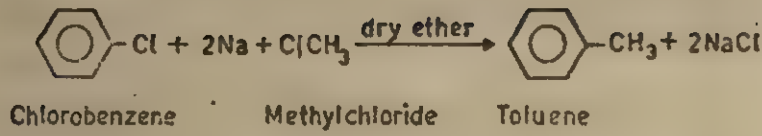
Alkyl halides react with sodium in dry ether to form higher alkanes. This reaction is known as **Wurtz reaction.**

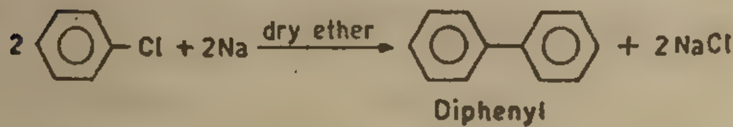
$$\underset{\text{Alkyl halide}}{2RX}+2Na\xrightarrow{\text{Dry ether}}\underset{\text{Alkane}}{R{-}R}+2NaX$$

For example :

$$\underset{\text{Methyl bromide}}{2CH_3Br}+2Na\xrightarrow{\text{Dry ether}}\underset{\text{Ethane}}{CH_3{-}CH_3}+2NaBr$$

When both alkyl and aryl (or only aryl) halides are treated with sodium, in dry ether, the reaction is called **Wurtz-Fittig reaction.**





(*iii*) Reduction

Halogenoalkanes may be reduced to alkanes by nascent hydrogen (obtained from Zn+HCl, Na/Hg+H_2O, *etc.*), hydrogen in

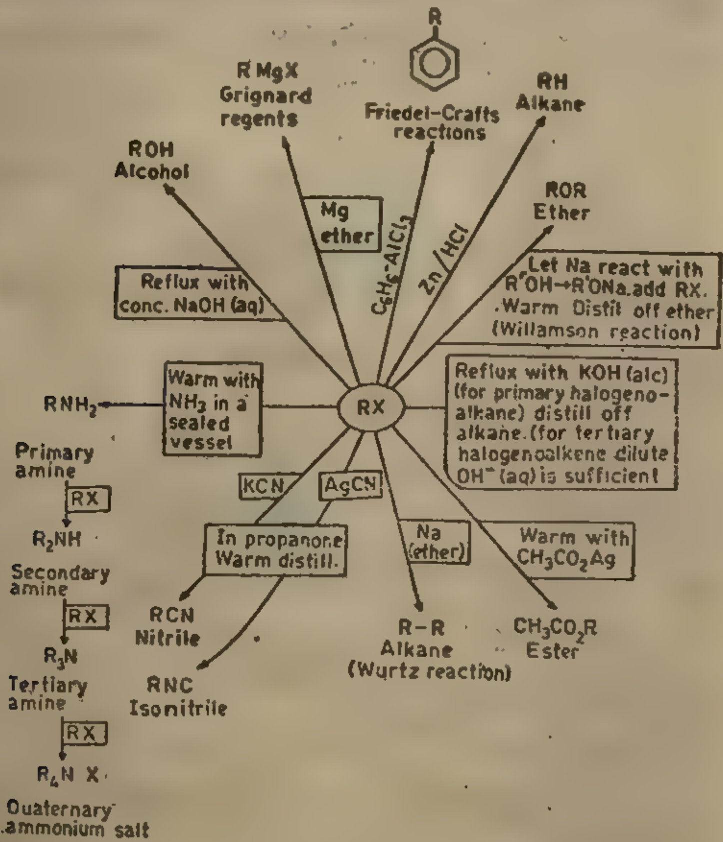


Fig. 7.4. Reactions of halogenoalkanes.

presence of catalyst (H_2/Pt, H_2/Ni, *etc.*), hydrogen iodide (or hydroiodic acid) in the presence of red phosphorus, *etc.*

$$\underset{\text{Alkyl halide}}{R{-}X} \xrightarrow{2H} \underset{\text{Alkane}}{RH} + HX$$

For example,

$$\underset{\text{Ethyl Chloride}}{C_2H_5Cl} + 2H \xrightarrow{Zn+HCl} \underset{\text{Ethane}}{C_2H_6} + HCl$$

Reductions of hologenoarenes is difficult.

The reactions of halogenoalkanes are portrayed in Fig. 7.4.

The possible reactions of chlorobenzene, a typical halogenoarene are given in Fig. 7.5.

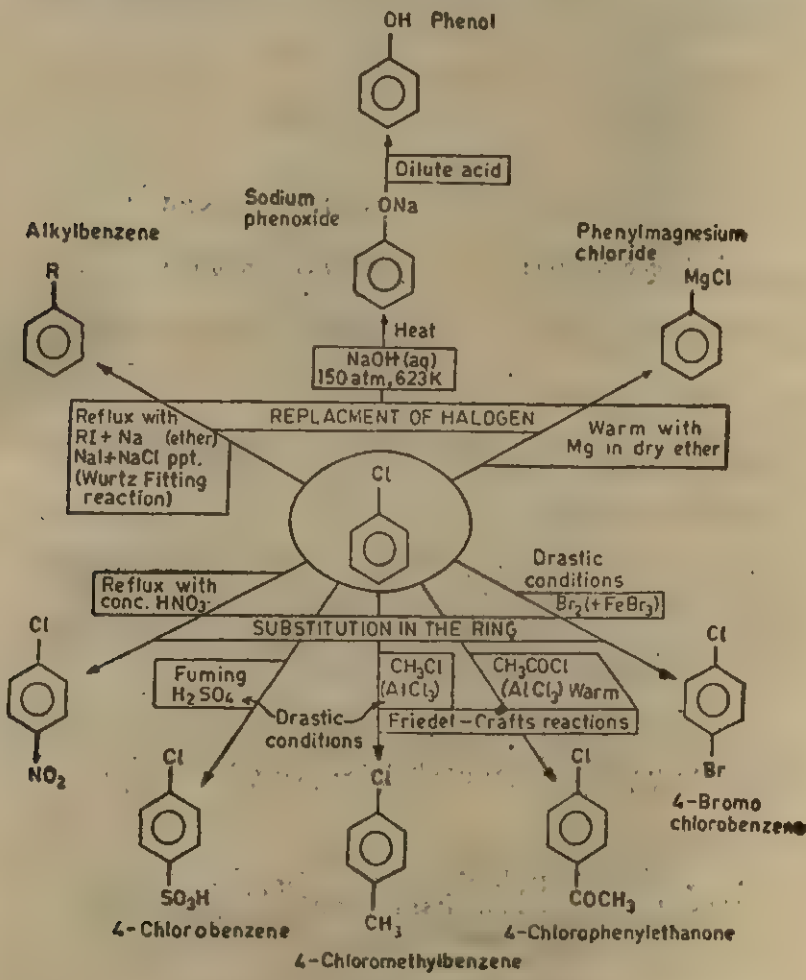


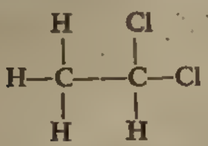
Fig. 7.5. Reactions of chlorobenzene.

7.4. DI-, TRI- AND POLY HALOGEN DERIVATIVES

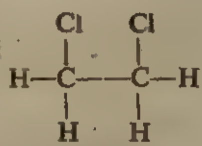
Though the term 'alkyl halides' refers generally to monohalogen derivatives of hydrocarbons yet some halogen derivatives containing two or more halogens are also important. Some of these are discussed here.

7.4.1. Dichloroethanes

Both the chlorines may be on the some carbon (1, 1-dichloroethane) or an different carbons (1, 2-dichloroethane). Two halogens on the same carbon are said to be in the gem-position. Whereas when two halogens are on adjacent carbon atoms, they are said to be in vicinal positions. Thus, the name and formula for the dichloroethanes are :



1, 1-Dichloroethane
or
Ethylidene chloride
or
Geminal or gem-dichloroethane



1, 2-Dichloroethane
or
Ethylene chloride
or
Vicinal or vic-dichloroethane

7.4.2. Trihalomethanes

These are trihalogen derivatives of methane and of these chloroform, $CHCl_3$ and iodoform, CHI_3 are important.

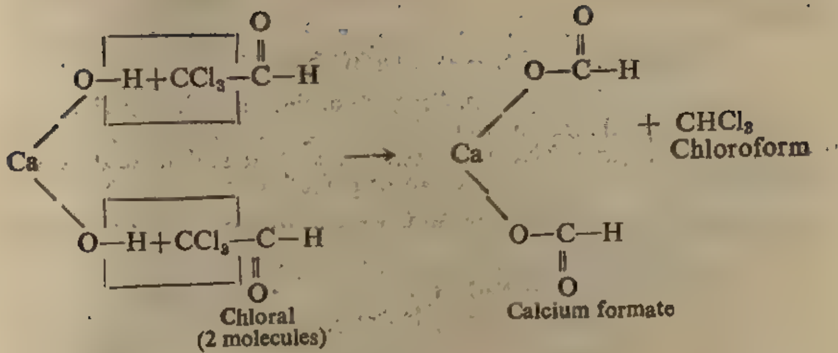
1. Chloroform, $CHCl_3$

Though pure $CHCl_3$ has been used as an inhalation anesthetic, but because of its toxicity, it is no longer extensively used for this purpose. **Since the discovery in 1976 that chloroform is a cancercausing agent (carcinogen)** it should no longer be permitted in cough remedies, tooth pastes, *etc.*

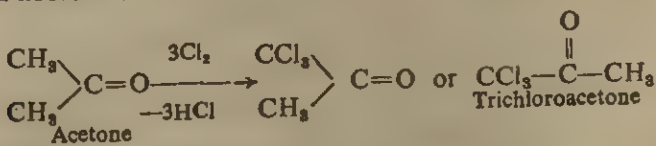
It is prepared from ethanol or acetone by heating with bleaching powder (a source of chlorine and calcuim hydroxide) or with chlorine and alkali. The reactions are complex but may be represented as under :

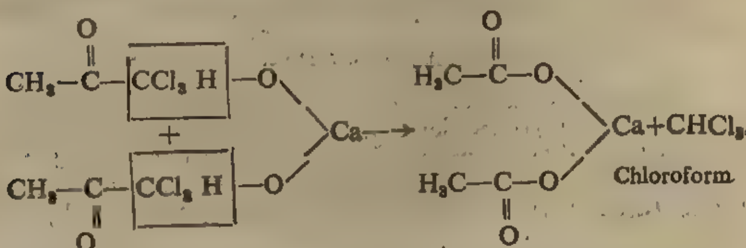
From ethanol :

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{Oxidation step} \atop -2HCl]{Cl_2} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[-3HCl]{3Cl_2} \underset{\text{Chloral}}{CCl_3.CHO}$$

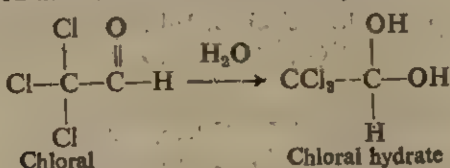


From acetone :





Though it is not commonly recommended as an anesthetic, pure chloroform is still sometimes used as such. Anaesthetic quality chloroform is readily obtained by distilling chloral hydrate with NaOH solution. For this purpose, chloral is separately prepared and stored as the stable dio-chloral hydrate :



Anaesthetic quality chloroform should not give a precipitate with $AgNO_3$ and is stored in dark (brown or blue) bottles to prevent its oxidation to poisonous phosgene :

$$2CHCl_3+O_2 \xrightarrow[+\text{Light}]{\text{Air}} 2COCl_2+2HCl$$

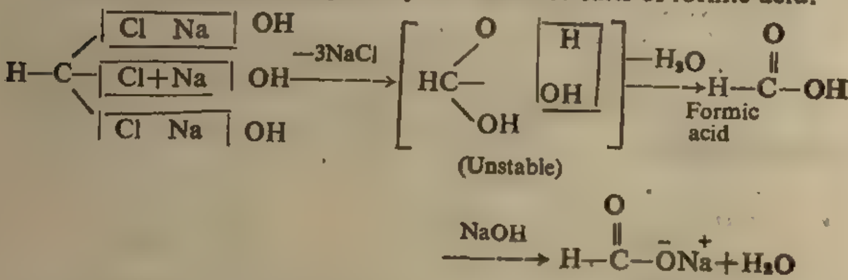
Traces of ethanol in chloroform inhibit this oxidation.

Alcohol converts the toxic phosgene to harmless diethyl carbonate

$$COCl_2+2C_2H_5OH \longrightarrow CO(OC_2H_5)_2+2HCl$$

Chloroform is a sweet smelling colourless liquid, *b p* 334K. It is sparingly soluble in water but readily dissolves in ether and alcohol. It is a good solvent for resins, oils, fats and waxes. It is used as a solvent in the manufacture of penicillin.

Haloforms are hydrolyzed by hot alkali to salts of formic acid.



Chloroform, on warming with silver powder, is converted to acetylene.

$$2CHCl_3+6Ag \longrightarrow CH\equiv CH+6AgCl$$

Chloroform is not inflammable but its vapours on ignition burn with a green-edged flame. Chloroform can be readily detected by the **isocyanide or carbylamine test,** which is carried out by warming chloroform with ethanolic sodium hydroxide and an amine (usually aniline). The product is easily identified by its foul smell.

$$C_6H_5-\ddot{N}H-H+Cl-CCl_2-H \xrightarrow{3NaOH} \underset{\text{(Isocyanide)}}{C_6H_5-N\rightleftarrows C}+3NaCl+3H_2O$$

The toxic isocyanide should be discarded into the sink only after hydrolysis with conc. hydrochloric acid.

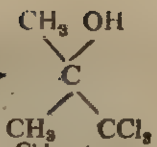
$$C_6H_5N\rightleftarrows C+2H_2O \xrightarrow[HCl]{Conc.} C_6H_5NH_2+HCOOH$$

Chloroform gives chloropicrin or nitrochloroform with conc. nitric acid.

$$\underset{\text{Chloroform}}{CHCl_3}+HNO_3 \longrightarrow \underset{\text{Chloropicrin}}{Cl_3C\,NO_2}+H_2O$$

In the presence of alkali chloroform undergoes condensation with acetone to form chloretone.

$$\underset{\text{Acetone}}{CH_3\,CO\,CH_3} + \underset{\text{Chloroform}}{CHCl_3} \longrightarrow$$



Chloretone

Uses : 1. Chloroform is used as anaesthetic. 2. It is used as a solvent for fats, rubber and iodine. 3. It is used as a laboratory reagent for testing primary amines. 4. It is used in the preparation of chloropicrin and chloretone. Chloropicrin is used as insecticide and chroretone is used as a hypnotic.

2. Iodoform, CHI_3

Iodoform is obtained by the action of iodine and alkali on acetone or alcohol.

With alcohol :

$$(i)\quad \underset{\text{Ethanol}}{C_2H_5OH} + I_2 \xrightarrow{\text{Heat}} \underset{\text{Acetaldehyde}}{CH_3\,CHO} + 2HI$$

$$\underset{\text{Acetaldehyde}}{CH_3\,CHO} + 3I_2 \xrightarrow{\text{Heat}} \underset{\text{Triiodoacetaldehyde}}{CI_3\,CHO} + 3HI$$

$$\underset{\text{Triiodoacetaldehyde}}{CI_3\,CHO} + KOH \xrightarrow{\text{Heat}} \underset{\text{Iodoform}}{CHI_3} + HCOOK$$

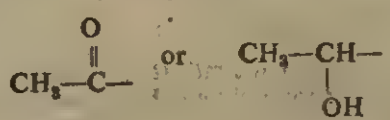
With acetone :

$$(ii)\quad \underset{\text{Acetone}}{CH_3\,CO\,CH_3} + 3I_2 \xrightarrow{\text{Heat}} \underset{\text{Triiodoacetone}}{CI_3\,CO\,CH_3} + 3HI$$

$$\underset{\text{Triiodoacetone}}{CI_3\,CO\,CH_3} + KOH \xrightarrow{\text{Heat}} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Pot. acetate}}{CH_3\,COOK}$$

In the laboratory, it is generally prepared by using sodium carbonate in place of sodium hydroxide. Sodium hypoiodide is produced during the reaction. This reaction involves the oxidation, halogenation and cleavage of carbon-carbon bond. This sequence of reactions, resulting from treatment with iodine and alkali, is known as the iodoform reaction. This reaction is used in qualitative organic analysis and is known as **iodoform test.**

Iodoform test : Compounds which contain either of the structural units



give a positive iodoform test. Thus, ethanol, acetaldehyde, acetone, propanone,2-propanol, and iso-propanol will give a positive test.

The test is performed by warming at 333K to 343K the substance, to be tested, with aqueous sodium carbonate and iodine solution. Thus, with alcohol,

$$CH_3CH_2OH + NaOI \xrightarrow{\text{Oxidation}} CH_3CHO + NaI + H_2O$$

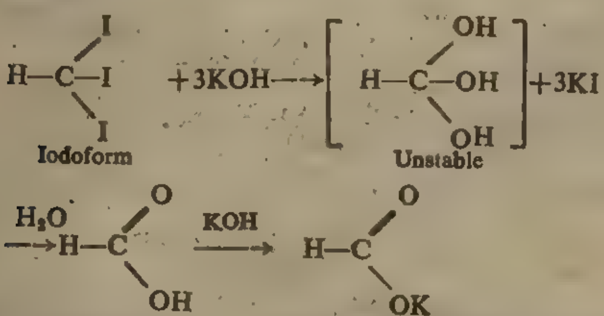
$$CH_3CHO + NaOI \xrightarrow{\text{Substitution}} CI_3CHO + 3NaOH$$

$$CI_3CHO + NaOH \xrightarrow{\text{Cleavage}} CHI_3 + HCOONa$$

Properties and chemical reactions

Iodoform is a pale yellow solid having hexagonal plate crystals (*mp* 392K). It has a characteristic smell. It is insoluble in water but soluble in ether and ethyl alcohol. Some chemical reactions are outlined below :

(*i*) **Hydrolysis** : When heated with aqueous alkali, formate is produced.



(*ii*) **With Ag powder** : Iodoform on heating with Ag powder gives acetylene.

$$\underset{\text{Iodoform}}{2CHI_3} + 6Ag \longrightarrow \underset{\text{Acetylene}}{CH{\equiv}CH} + 6Ag\,I$$

Uses : It is used as an antiseptic for dressing of wounds.

7.4.3 Dichlorodifluoromethane or Freon, CCl_2F_2

On passing anhydrous hydrogen fluoride through carbon tetrachloride using antimony pentachloride, $SbCl_5$ as a catalyst, freon is formed.

$$CCl_4 + 2HF \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl$$

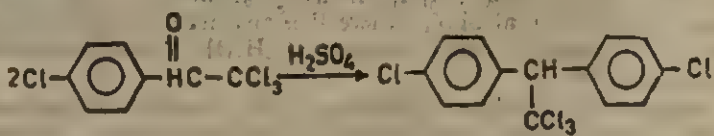
Freon is a stable and inert compound. It is an ideal refrigerant; it is non-toxic, non-corrosive, non-inflammable, almost odourless, boils at 243K and does not decompose below 773K. It is widely

used as the propellant gas in aerosol sprays. The presence of freon in the upper part of the atmosphere has been found to help the destruction of the ozone layer. Efforts are being made to reduce its use.

7.4.4. DDT, [2, 2—bis (p-chloro phenyl) —1, 1, 1—trichloro-ethane]

DDT is a polychlorinated hydrocarbon whose use as a pesticide has been criticised because of the possible toxicity to human beings and animals associated with continuous exposure to it. Its extreme stability results in its persistence in the environment for a long time, and thus it tends to concentrate in fatty tissues. Its long term effects have been found to be dangerous. Its use has been banned in some of the countries.

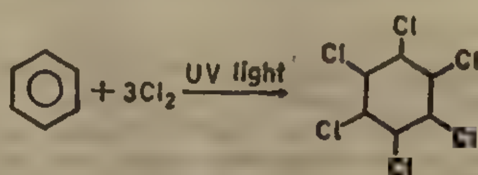
The trade name DDT is based upon its earlier name (which is incorrect) dichlorodiphenyl trichloroethane. The chloro hydrocarbon DDT is prepared from inexpensive starting materials, chlorobenzene and trichloroacetaldehyde. The reaction is catalyzed by acid.



D.D.T.

7.4.5. Benzene hexachloride or BHC, $C_6H_6Cl_6$

BHC is used as a powerful insecticide. Its trade name is **gammexane lindane** N 666. It is extensively used as a pesticide in agriculture. It is manufactured by passing chlorine through boiling benzene in bright sunlight, or in ultraviolet light.



7.4.6. Carbon Tetrachloride, CCl_4

Carbon tetrachloride is manufactured by reacting **carbon** disulphide with chlorine in the presence of an anhydrous iron (III) chloride catalyst.

$$CS_2+3Cl_2 \longrightarrow CCl_4+S_2Cl_2$$

Carbon tetrachloride is a colourless sweet smelling non-inflammable liquid.

Because its vapours are non-inflammable, it is an important industrial solvent and is also used as a fire extinguisher under the name of pyrene'. At high temperatures, in presence of water vapours it forms carbonyl chloride which is extremely toxic.

$$CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl$$

Hence after use of pyrene fire extinguisher, the rooms should be thoroughly ventilated.

On passing vapours of anhydrous HF through CCl_4, using $SbCl_5$ as a catalyst, dichlorodifluoromethane is formed.

$$CCl_4 + 2HF \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl$$

It is used in the production of fluorinated hydrocarbons.

PART II

(ALCOHOLS AND PHENOLS)

7.5 Introduction

The general formula for the monohydric alcohols is $C_nH_{2n+1}OH$ (or ROH). They may be regarded as alkane derivatives in which hydrogen is replaced by the hydroxyl group. RH, the alkane becomes ROH, the alcohol, where R is any alkyl group or benzyl group, for example, ethyl alcohol C_2H_5OH, benzyl alcohol $C_6H_5CH_2OH$, *etc.*

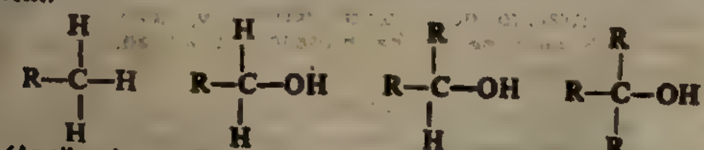
Alcohols are classified according to the number of hydroxyl groups in the molecule as monohydric (one —OH group), dihydric (two—OH groups) trihydric (three—OH groups), *etc.* Glycol is an example of dihydric alcohols and glycerol is an example of trihydric alcohols. When four or more hydroxyl groups are attached, they are called polyhydric alcohols.

$C_2H_5—OH$ — Ethanol (A monohydric alcohol)

$CH_2—OH$ | $CH_2—OH$ — Glycol (A dihydric alcohol)

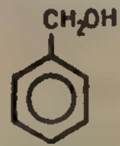
$CH_2—OH$ | $CH—OH$ | CH_2OH — Glycerol (A trihydric alcohol)

Monohydric alcohols are further classified as primary, secondary and tertiary according as they contain one, two, or three alkyl groups attached to the alcohol carbon (the carbon to which hydroxyl group is attached). These alkyl groups may be same or different.



(An alkane) (Primary alcohol) (Secondary alcohol) (Tertiary alcohol)

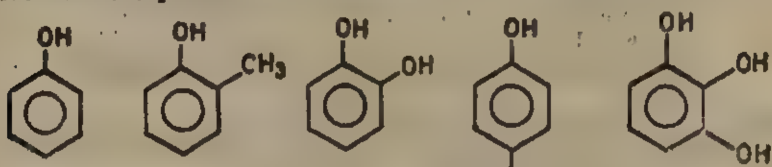
An aromatic alcohol is an aromatic compound that contains the hydroxyl group attached to a side chain :



Benzylalcohol
(Aromatic alcohol)

Its properties are more like that of an alcohol than a phenol. A phenol is an aromatic compound containing hydroxyl group attached to an aromatic ring.

Phenols are aromatic compounds in which $-OH$ group is substituted directly on the benzene ring. The compounds are classified as mono-, di- and trihydric phenols according to the number of $-OH$ groups contained in their molecules. Phenol and its derivatives, such as o-cresol, catechol, pyrogallol and nitrophenol are typical aromatic compounds.



Phenol o-Cresol
(Monohydric) Catechol p-Nitrophenol Pyrogallol
(Dihydric) (Trihydric)

7.6. NOMENCLATURE

The lower alcohols are better known by their common (trivial) names which are based on the name of the alkyl chain :

$CH_3—OH$ Methyl alcohol

$C_2H_5—OH$ Ethyl alcohol

$CH_3—CH_2—CH_2—OH$ *n*-Propyl alcohol

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$$
Isopropyl alcohol

$$CH_3\,CH_2-\underset{\displaystyle CH_3}{\underset{|}{CHOH}}$$
sec-Butyl alcohol

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$$
tert-Butyl alcohol

In IUPAC system,

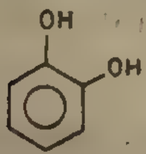
1. Alcohols are named as alkanols and the name of the alcohol is derived by substituting the terminal 'e' of the parent alkane by 'ol'.

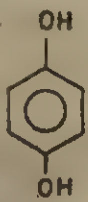
2. The longest chain containing the functional group is chosen as the parent chain.
3. Numbering is done from that end which gives the lowest number to the hydroxyl functional group.
4. The position of the hydroxyl group and other substituents are indicated by numbers.

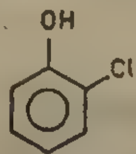
For example :

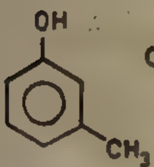
Alcohol	*Parent hydrocarbon*	*Name*
$\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$	$CH_3-CH_2-CH_2-H$	1-Propanol
$\begin{matrix}\overset{1}{CH_3} \\ \overset{3}{CH_3}\end{matrix}\!\!>\overset{2}{CH}-OH$	$\begin{matrix}CH_3 \\ CH_3\end{matrix}\!\!>CH-H$	2-Propanol
$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{OH}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_3}$	$CH_3-CH_2-\underset{H}{CH}-CH_2-CH_3$	3-Pentanol
$\overset{3}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{1}{CH_2}-OH$	$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-H$	2, 2-Dimethyl-1-propanol
$\overset{4}{CH_3}-\underset{CH_3}{\overset{3}{CH}}-\underset{OH}{\overset{2}{CH}}-\overset{1}{CH_3}$	$CH_3-\underset{CH_3}{CH}-\underset{H}{CH}-CH_3$	3-Methyl-2-butanol

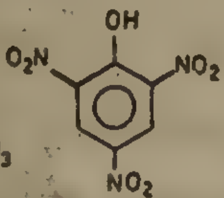
Phenols are named as the derivatives of the simplest compound, 'phenol'. Trivial names are frequently used.

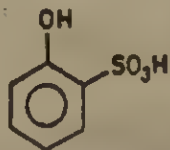

Catechol


Quinol


o-Chlorophenol


m-Cresol


2,4,6-Tri-nitrophenol


o-Phenol sulphonic acid

Isomerism. The three classes of alcohols arising as a result of differences in the position of the hydroxyl in the molecule are examples of a type of isomerism known as **position isomerism.** Alcohols also show **chain isomerism** due to the different structures of the carbon chain. The four positional isomers of butyl alcohols (C_4H_9CH) are :

$$(i)\quad \overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-OH$$

n-Butyl alcohol ; 1-Butanol

$$(ii)\quad \begin{array}{c} \overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H-\overset{1}{C}H_3 \\ \qquad\quad | \qquad \\ \qquad\quad OH \qquad \end{array}$$

sec-Butyl alcohol ; 2-Butanol

$$(iii)\quad \begin{array}{c} \overset{3}{C}H_3-\overset{2}{C}H-\overset{1}{C}H_2-OH \\ | \qquad\qquad \\ CH_3 \qquad\qquad \end{array}$$

Isobutyl alcohol ; 2-Methyl-1-propanol

$$(iv)\quad \begin{array}{c} 1\ CH_3 \\ | \\ H_3C-C-OH \\ | \\ 3\ CH_3 \end{array}$$

tert-Butyl alcohol ; 2-Methyl-2-propanol

Alcohols (*i*) and (*iii*) also exhibit chain isomerism.

Alcohols also show functional isomerism. For example, alcohol with molecular formula C_2H_6O also represents diethyl ether.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \qquad\qquad \underset{\text{Diethyl ether}}{CH_3-O-CH_3}$$

Higher alcohols, like amyl alcohol show optical isomerism also.

7.7. ALCOHOLS AND PHENOLS

7.7.1. Preparation of Alcohols

Alcohols can be prepared by the following general methods :

(*i*) **By hydrolysis of a alkyl halides.** An alkyl halide on hydrolysing with an aqueous alkali or moist silver oxide yields alcohols.

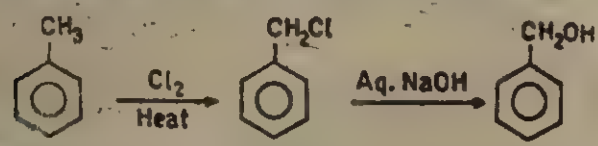
$$\underset{\text{Alkyl halide}}{RX} + NaOH \longrightarrow \underset{\text{Alcohol}}{R-OH} + NaX$$

For example :

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + NaOH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KBr$$

One limitation of the method is that though a primary alkyl halide gives a good yield of the alcohol, a tertiary alkyl halide is

mostly converted to an alkene. A second limitation is that the alkyl halides are most easily obtainable from the corresponding alcohols itself. However, it is a good method to prepare benzyl alcohol by the following steps :



Toluene — Benzyl chloride — Benzyl alcohol

(*ii*) **From aldehydes and ketones.** The methods used are given below :

By direction reduction. Since aldehydes and ketones are oxidation products of alcohols, the latter can be prepared from the former with reducing agents. The reagents used are $LiAlH_4$ (in etheral solution), sodium borohydride ($NaBH_4$) sodium and ethanol or hydrogen in the presence of a catalyst like Ni, Pt or Pd. Carbonyl group ($>C=O$) compounds—aldehydes and ketones can be reduced to primary and secondary alcohols respectively.

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\displaystyle H}{\overset{|}{C}}=O}+2[H]\xrightarrow{(Pt)}\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH}$$

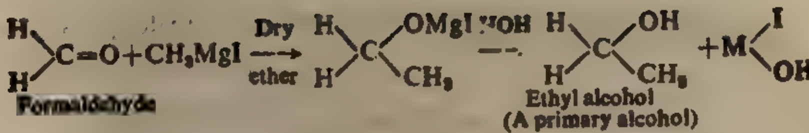
$$\underset{\text{Acetone}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O}+2[H]\xrightarrow{(Pt)}\underset{\text{Isopropyl alcohol}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH}$$

Tertiary alcohols cannot be made by reduction.

By Grignard reagent. Aldehydes and ketones may be converted to higher alcohols by using Grignard reagent. This method may be used to prepare all the three classes of alcohols. The overall reaction is as follows :

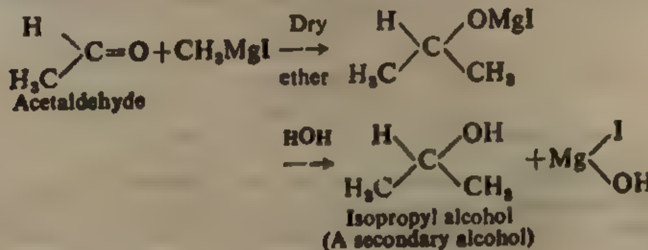
$$\underset{\text{Carbonyl compound}}{>C=O}+\underset{\text{Grignard reagent}}{RMgX}\xrightarrow[\text{ether}]{\text{Dry}}\underset{\substack{\text{Addition product}\\\text{(a complex mag-}\\\text{nesium alkoxide)}}}{>C<^{OMgX}_{R}}\xrightarrow[\text{Acid}]{\text{HOH}}\underset{\text{Alcohol}}{>C<^{OH}_{R}}+Mg<^{X}_{OH}$$

Primary alcohols are obtained using formaldehyde :



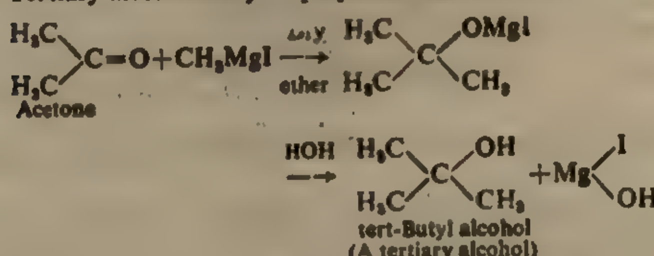
This reaction is particularly useful for increasing the carbon chain by one carbon atom.

Secondary alcohols are obtained from aldehydes other than formaldehyde :



This reaction is also useful for increasing the carbon chain by one carbon atom.

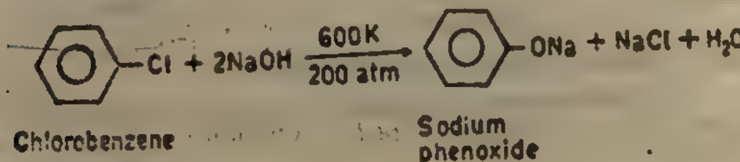
Tertiary alcohols may be prepared from ketones :



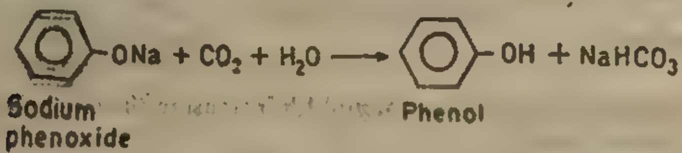
7.7.2. Preparation of Phenols

Phenols are generally prepared by the following methods :

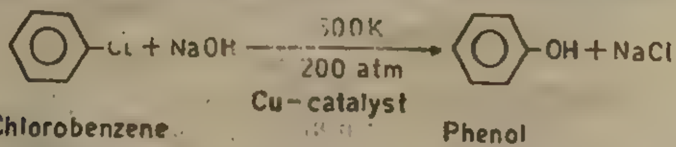
(*i*) **From chlorobenzene**. Phenol is obtained on a large scale by hydrolysing chlorobenzene with 10% NaOH at about 600K and high pressures.



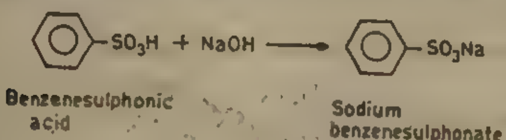
The phenol is liberated when carbon dioxide under pressure is passed through the solution.

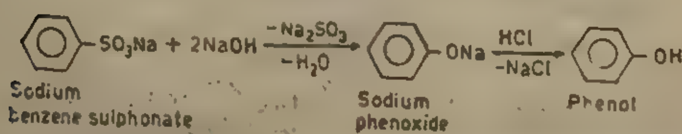


HCl can also be used in place of CO_2. In the presence of copper catalyst, phenol can be obtained directly (Dow's process).



(*ii*) **From benzenesulphonic acid.** Phenol is manufactured by this method. Both benezenesulphonic acid and sodium hydroxide are fused. The fused mass is dissolved in water, and the phenol (present as sodium phenoxide in the solution) is liberated on acidification.





(*iii*) **From benzene diazonium salt.** Phenol is obtained by boiling (steam distillation) benzene diazonium salt with dilute acid. The salt is obtained from aniline by treatment with nitrous acid at low temperature (273-278 K).

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[\text{HCl}]{\text{NaNO}_2} \underset{\text{Benzene diazonium salt}}{C_6H_5N_2^+\,Cl^-} + H_2O \xrightarrow[\text{dil. HCl}]{\text{Boil}} \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

7.7.3. Industrial Preparation of Alcohols

(*i*) **By hydration of alkenes :** Alkenes are obtained by cracking of petroleum and are separated from the mixture by fractionation.

Ethyl alcohol can be prepared by absorbing ethylene gas in concentrated sulphuric acid under pressure when ethyl hydrogen sulphate and ethyl sulphate are formed.

For example :

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + (HO)_2SO_2 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3{-}CH_2{-}OSO_2OH}$$

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5O\ SO_2OH} + C_2H_4 \longrightarrow \underset{\text{Ethyl sulphate}}{(C_2H_5O)_2SO_2}$$

The reaction mixture on boiling with water gives alcohols.

For example :

$$C_2H_5OSO_2OH + H_2O \longrightarrow C_2H_5OH + H_2SO_4$$

$$(C_2H_5O)_2SO_2 + 2H_2O \longrightarrow 2C_2H_5OH + H_2SO_4$$

This is the basis for manufacturing ethyl alcohol. Some diethyl ether is formed as a by-product. Addition of H_2SO_4 to propylene followed by hydrolysis gives a secondary alcohol.

$$\underset{\text{Propylene}}{CH_3{-}CH{=}CH_2} + H_2SO_4 \rightarrow \underset{\substack{\text{Isopropyl}\\ \text{hydrogen sulphate}}}{CH_3{-}\overset{\overset{\displaystyle OSO_2OH}{|}}{CH}{-}CH_3} \xrightarrow[-H_2SO_4]{H_2O} \underset{\substack{\text{Isopropyl}\\ \text{alcohol}}}{CH_3\overset{\overset{\displaystyle OH}{|}}{CH}CH_3}$$

Among primary alcohols, only ethyl alcohol can be prepared by this method (Markovnikov's rule).

This method is suitable for the preparation of secondary and tertiary alcohols.

Alkenes, that form secondary and tertiary alcohols, can also be converted into primary alcohols by hydroboration with diborane (B_2H_6) followed by oxidation of the alkylborane so produced with alkaline H_2O_2.

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + (HBH)_2 \longrightarrow \underset{\text{n-Propylborane}}{CH_3{-}CH_2{-}CH_2BH_2}$$

$$\xrightarrow{\text{Alkali } H_2O_2} \underset{\text{n-Propyl alcohol}}{CH_3{-}CH_2{-}CH_2OH}$$

The hydroboration-oxidation of alkenes does not follow Markovnikov's rule and is an important method for obtaining primary alcohols.

(*ii*) **Fermentation methods** : The fermentation of sugars by yeast to prepare alcoholic beverages has been long known. Yeast

contains the enzymes*, invertase and zymase which catalyze the conversion of sucrose as follows :

From molasses : This is an important source for alcohol :

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}+H_2O} \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH+2CO_2$$

From starch : Starch (from potatoes, maize, *etc.*) is another important source for the preparation of alcohol. Starch, which is a polymer of glucose units is first broken down to a dimer (maltose) by treatment with an enzyme called diastase.

$$2(C_6H_{10}O_5)_n+nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

Maltose solution so obtained is fermented with yeast (as in the case of molasses) to get ethyl alcohol.

$$C_{12}H_{22}O_{11}+H_2O \xrightarrow[\text{yeast}]{\text{Maltase in}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{in yeast}]{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5—OH}+2CO_2$$

The fermented liquor is subjected to fractional distillation to obtain alcohol.

(*iii*) **Oxo method** : Alkenes react with water gas ($CO+H_2$) in the presence of $[Co(CO)_4]_2$ (catalyst) at high temperature and pressure to yield aldehydes. Reduction of an aldehyde using sodium amalgam and water (or by catalytic hydrogenation) give primary alcohol.

$$CH_2=CH_2+\underbrace{CO+H_2}_{\text{Water gas}} \xrightarrow{[CO(CO)_4]_2} CH_3CH_2CHO$$

$$\xrightarrow{H_2/Ni} CH_3CH_2CH_2OH$$

7·7·4. Industrial Preparation of Phenol

Phenol can be obtained from coal-tar and by synthesis.

(*i*) **From coal-tar** : A number of phenols are present in coal-tar and can be obtained from the middle-oil and heavy-oil fractions obtained by coal-tar distillation.

*Enzymes are organic catalysts and are very specific in their action.

(*ii*) **Synthetic method :** Phenol is manufactured by two methods :

1. Sodium benzene sulphonate is hydrolyzed with alkali, phenol is librated on acidifying with HCl.

2. Chlorobenzene can be hydrolyzed by sodium hydroxide but only under drastic conditions of high temperatures and pressures.

Some of the typical methods for the preparation of ethanol are given in Fig. 7.6.

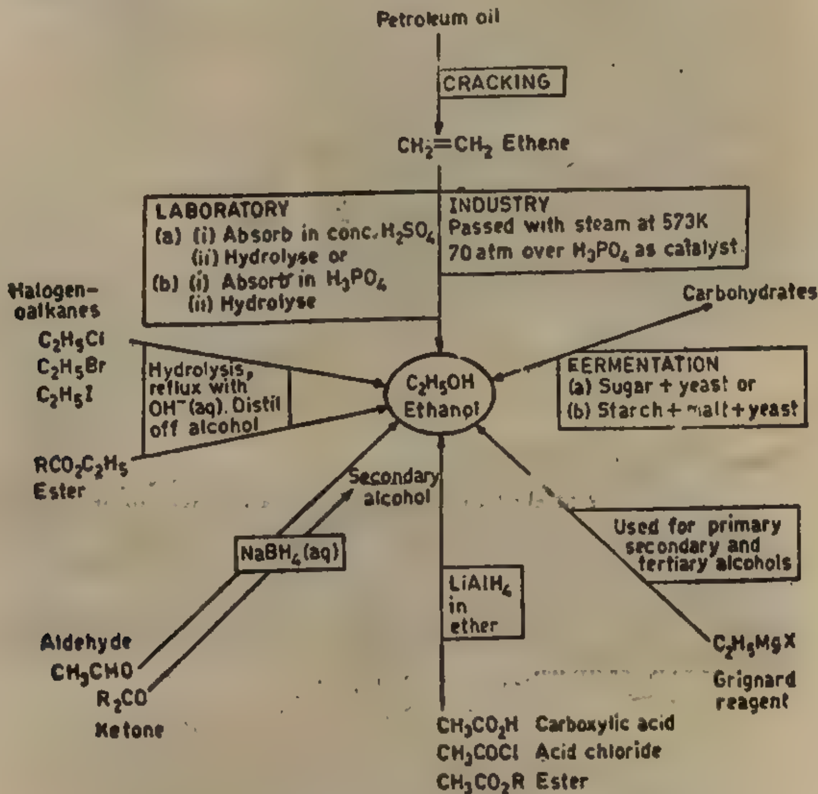


Fig. 7.6. Methods of preparing ethanol, a typical alcohol.

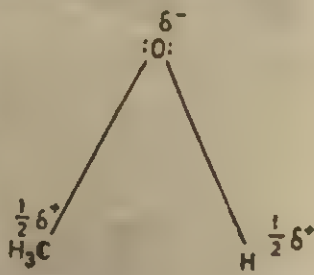
7.7.5. The nature of –OH group

The –OH group in alcohol

In –OH, the oxygen has six electrons, two of them unpaired, in its outer shell. In the alcohols, one of the unpaired electrons of oxygen is bonded covalently to a carbon atom, the other to

hydrogen : $-C \times \cdot\ddot{\underset{..}{O}}\cdot \times H$. The introduction of the highly electro-negative oxygen atom significantly changes the properties of the hydrocarbon. The molecules become polar, as charge centres develop in the neighbourhood of oxygen.

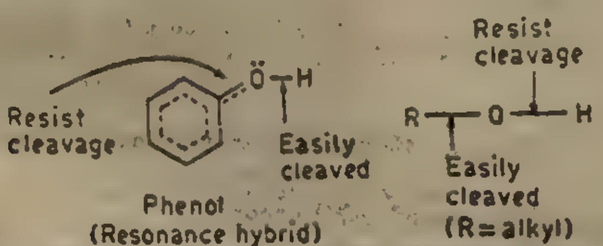
All hydroxyl groups show acidic properties to a certain degree. They are acidic by virtue of the fact that hydrogen atom of the —OH group can be removed as H^+ by bases. The skeleton to which the group is attached, however, will influence the 'ease' with which protons can be removed. The acid character decreases as we move from a primary to secondary to tertiary alcohol because of increasing number of alkyl groups. Because the oxygen atom of the hydroxyl groups has lone pair of electrons, it is in principle possible for it to accept a proton from a stronger atom—in other words to behave as a base.



$$-\ddot{\underset{..}{O}}-H + H^+ \longrightarrow -\overset{\overset{\displaystyle H}{|}}{\underset{..}{O^+}}-H$$

The —OH group in phenol

A lone pair of electrons associated with the oxygen of phenolic —OH interacts with the π-system of the benzene ring and is delocalized over the entire molecule. As a result of delocalization of electrons, the —C—O— bond acquires some double character and becomes stronger than —O—H σ-bond. Also the increased electron density in the benzene ring activates it, and gives electrophillic substitution reactions.



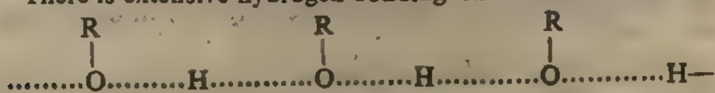
In alcohols, no resonance is thus possible. The non-bonded electrons remain localized on the oxygen atom. The $-C\overset{\sigma}{-}OH$ lin-

kage retains its σ-bond character and is weak as compared to that in phenols.

7.7.6. Properties and Reactions of Alcohols

As already mentioned alcohols are composed of a non-polar hydrocarbon part and the polar —OH group. Both the parts influence the properties of the alcohols. The lower alcohols are colourless liquids having a characteristic odour and burning taste. The higher members are colourless solids with no characteristic smell and taste.

There is extensive hydrogen bonding in alcohols resulting in

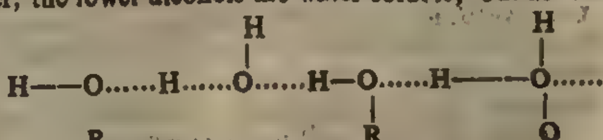


Hydrogen bonding amongst alcohols

high boiling points, much higher than corresponding alkyl halides or alkanes. The boiling points of alcohols increase as the molecular mass increases. For example, CH_3OH, 338K ; C_2H_5CH, 351K. Branched chain alcohols have lower boiling points than the isomeric straight chain molecules. The boiling points of alcohols increase fairly regularly with the addition of each $—CH_2$ group to the hydrocarbon chain. This is illustrated by taking example of butyl alcohol (C_4H_9OH).

Compound Name	Formula	*bp*/K
n-Butane	$CH_3—CH_2—CH_2—CH_3$	267
n-Butyl bromide	$CH_3CH_2CH_2CH_2Br$	374.6
n-Butyl alcohol	$CH_3CH_2CH_2CH_2OH$	391
Isobutyl alcohol	$CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{\vert}{CH_2OH}}$	381
sec-Butyl alcohol	$CH_3—\underset{\displaystyle OH}{\underset{\vert}{CH_2}}—CH—CH_3$	373
tert-Butyl alcohol	$CH_3—\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}—OH$	353

Again due to presence of hydrogen bonding between alcohol and water, the lower alcohols are water soluble, but as the contri-



Hydrogen bonding between water and alcohol

bution of the alkyl chain (which is water repelling) increases in higher alcohols, these are water insoluble. The fall in solubility of higher alcohols is due to the fact that the large repulsive effect of non-polar part of alcohol outweighs the solubility effect of —OH group. The higher alcohols are soluble in organic solvents.

Chemical reactions of alcohols

Chemical reactions of alcohols can be divided into two types :

(*a*) Involving break up of carbon-oxygen bond (C—⋮—OH)

(*b*) Involving break up of the oxygen-hydrogen bond (C—O—⋮—H).

(*a*) **Reactions involving break up of carbon-oxygen bond** (C—⋮—OH)

(*i*) **Reaction with halogen acids :** On heating an alcohol with halogen acids (HX), halides are obtained,

$$\underset{\text{Alcohol}}{R{-}OH} + HX \longrightarrow \underset{\text{Alkylhalide}}{RX} + H_2O \ (X{=}Cl, Br, I)$$

For example :

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + HCl \xrightarrow[-H_2O]{\text{Anhydrous } ZnCl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O$$

The reaction is believed to proceed via formation of a protonated alcohol (alcohol acts as weak base). The positive charge on oxygen weakens the C—OH bond leading to its cleavage. As a result, the oxonium ion dissociates into water and carbonium ion. The carbonium ion then combines with a halide ion to form the alkyl halide.

$$\underset{\text{Alcohol}}{R{-}O{-}H} + H^+ \longrightarrow \underset{\text{(Protonated alcohol)}}{R{-}\overset{\overset{\displaystyle H}{|}}{O^+}{-}H} \longrightarrow \underset{\text{Carbonium ion}}{R^+} \xrightarrow{X^-} \underset{\text{Alkyl halide}}{RX}$$

The order of reactivity of alcohols is :

$$C_6H_5CH_2OH > (CH_3)_3C{-}OH > (CH_3)_2\ CHOH > CH_3CH_2OH$$

The relative reactivity of the acids is in the order HI>HBr>HCl (I^- is a better nucleophile than Br^- and, in turn, Br^- is better than Cl^-). Good yields of alkyl halides are obtained by using some dehydrating agent (*e.g.*, anhydrous $ZnCl_2$) which can remove water from the reaction mixture.

(*ii*) **Reaction with phosphorus halides and thionyl chloride :** Alcohols are converted to the corresponding chlorides and bromides by reaction with phosphorus trichloride or tribro-

mide respectively. The chlorides may also be prepared by reaction with thionyl chloride in the presence of pyridine, which has the advantage that only gaseous by-products are formed.

$$\underset{\text{Alcohol}}{ROH} + PX_3 \dashrightarrow \underset{\text{Alkyl halide}}{RX} + H_3PO_3\ (X = Cl, Br)$$

For example :

$$\underset{\text{Ethanol}}{3CH_3CH_2OH} + PX_3 \dashrightarrow \underset{\text{Ethyl halide}}{3CH_3CH_2X} + H_3PO_3$$

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + SO_2 + HCl$$

Phosphorus penthalides (PX_5) also give the corresponding halides *e.g.*, $ROH + PX_5 \rightarrow RX + POX_3 + HX$.

(*iii*) **Dehydration of alcohols :** Alcohols on dehydration yield alkenes.

The dehydration may be carried out either by (*a*) heating with conc. sulphuric acid at 443K or (*b*) passing the alcohol vapours over alumina, Al_2O_3, at 623-673K. In place of sulphuric acid, or the phosphoric acid H_3PO_4 can also be used.

The ease of dehydration of the alcohols is in the order :

tertiary > secondary > primary

The reaction is believed to proceed by initial formation of a protonated alcohol, which dissociates into water and a carbonium ion ; the carbonium ion in turn loses a proton to yield an alkene.

$$\underset{\text{Alcohol}}{CH_3-CH_2-OH} \xrightarrow{+H^+} \underset{\text{Protonated alcohol}}{CH_3-CH_2-O^+H_2} \xrightarrow{-H_2O} \underset{\text{Carbonium ion}}{(CH_3-CH_2)^+} \xrightarrow{-H^+} \underset{\text{Alkene}}{CH_2=CH_2}$$

In the course of dehydration, different products may be obtained depending on the reaction conditions. For example, when dehydration is effected at 383K,

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \xrightarrow{383K} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5OSO_2OH} + H_2O$$

Ethyl hydrogen sulphate can be distilled under reduced pressure to obtain diethyl sulphate.

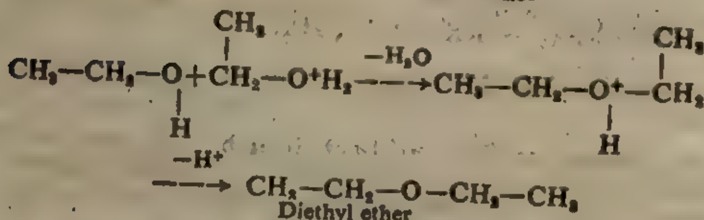
$$\underset{\text{Ethyl hydrogen sulphate}}{2C_2H_5OSO_2OH} \dashrightarrow \underset{\text{Diethyl sulphate}}{(C_2H_5O)_2SO_2} + H_2SO_4$$

In the course of dehydration, if the temperature used is < 413K and the amount of alcohol used is more than one equivalent of H_2SO_4, then one molecule of water may be eliminated per two molecules of alcohol to yield ether.

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5OSO_2OH} + HOC_2H_5 \xrightarrow{<413K} \underset{\text{Ether}}{C_2H_5OC_2O_5} + H_2SO_4$$

It is believed that in the above reaction, an unprotonated alcohol molecule reacts with a protonated alcohol molecule.

$$CH_3CH_2OH + H^+ \longrightarrow \underset{\text{Oxonium ion, protonated alcohol}}{CH_3CH_2O^+H_2}$$



When headed to 433—443K in the presence of conc. H_2SO_4, dehydration of alcohol takes place forming alkene.

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5O\ SO_2\ OH} \xrightarrow{433-443K} \underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2SO_4$$

The reaction proceeds as follows :

$$H{-}CH_2{-}CH_2{-}OH + H^+ \longrightarrow H{-}CH_2{-}CH_2{-}O^+H_2$$

$$\xrightarrow{-H_2O} H{-}CH_2{-}C^+H_2 \xrightarrow{-H^+} \underset{\text{Ethene}}{CH_2{=}CH_2}$$

Phenols, being acidic in nature, do not experience substitution of —OH groups like alcohols.

(b) Reactions involving break up (cleavage) of oxygen-hydrogen (C—O—|—H) bond

(*i*) **Alcohols as acids :** In the conversion of alcohols to either alkyl halides or alkenes, the first step was the protonation of the alcohol, acting as a base. Alcohols are also capable of acting as acids by the loss of a hydrogen ion to form the alkoxide ion RO^-. Alcohols react with active metals such as sodium, potassium and magnesium to form metal alkoxides, RO^-M^+ and $(QO^-)M^{2+}$. Alcohols behave as weak acids, like water.

$$\underset{\text{Alcohol}}{R{-}OH} \oplus Na \longrightarrow \underset{\text{Sodium alkoxide}}{RO^-Na^+} + \tfrac{1}{2}H_2$$

For example :

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5ONa} + H_2$$

The order of reactivity of different alcohols is : primary > secondary > tertiary and hence, the acid character also decreases according to the order. Other reagents like, metal hydrides, metal amides and Grignard reagents also react with alcohols to form metal alkoxides.

(*ii*) **Oxidation of alcohols** : Primary, secondary and tertiary alcohols when oxidized give different products, and this provides a means for distinguishing between them. The oxidation may be carried out by acid dichromate or alkaline permanganate or dilute HNO_3 or by heated copper.

A primary alcohol can be oxidized first to an aldehyde and then to a carboxylic acid both containing the same number of carbon atoms. For example, ethyl alcohol is oxidized by acidified potassium dichromate to acetaldehyde and then to acetic acid.

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} + [O] \xrightarrow[-H_2O]{\text{Acidified } K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + [O] \xrightarrow{\text{Acidified } K_2Cr_2O_7}$$

$$\underset{\text{Acetic acid}}{CH_3-C{\scriptstyle\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}}}$$

The reaction can be stopped at the aldehyde stage by using the proper oxidizing agent and distilling away the product as soon as it is formed.

However, the stronger oxidizing agent such as alkaline permanganate oxidizes it directly to acetic acid.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{\text{Alkaline } KMnO_4} \underset{\text{Acetic acid}}{CH_3COOH}$$

Secondary alcohols are oxidized to ketones, with the same number of carbon atoms as the original alcohol, which resist further oxidation. If drastic conditions are employed the ketones are broken down to acids with fewer carbon atoms than the original alcohol. For example :

$$\underset{\text{Isopropyl alcohol}}{\begin{matrix}CH_3\searrow\\ \quad CHOH\\ CH_3\nearrow\end{matrix}} \xrightarrow[-H_2O]{+[O]} \underset{\text{Acetone}}{\begin{matrix}CH_3\searrow\\ \quad C=O\\ CH_3\nearrow\end{matrix}} \xrightarrow[-CO_2,\ -H_2O]{+4[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

Tertiary alcohols resist oxidation in neutral or alkaline

medium. However, these are oxidized in acidic medium to a mixture of ketone and acid each containing fewer carbon atoms than the original alcohol.

$$R_3C\text{—}OH \xrightarrow[KMnO_4]{\text{Alkaline Neutral}} \text{No oxidation}$$

$$\underset{\text{tert-Butyl alcohol}}{(CH_3)_3C\text{—}OH} \xrightarrow[-CO_2,\ -H_2O]{+4[O]/HNO_3} \underset{\text{Acetone}}{(CH_3)_2C{=}O} \xrightarrow[-CO_2,\ -H_2O]{+4[O]/HNO_3} \underset{\text{Acetic acid}}{CH_3\text{—}COOH}$$

Catalytic dehydrogenation : Primary alcohols are oxidized to aldehydes by passing their vapours over heated metal catalyst (Cu or Ag) by a dehydrogenation reaction.

$$\underset{\text{Ethyl alcohol}}{CH_3\text{—}CH_2\text{—}OH} \xrightarrow[573\ K]{Cu} \underset{\text{Acetaldehyde}}{CH_3\text{—}CHO} + H_2$$

Secondary and tertiary alcohols behave differently :

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow[573\ K]{Cu} \underset{\text{Acetone}}{(CH_3)_2C{=}O} + H_2$$

$$\underset{\text{tert-Butyl alcohol}}{(CH_3)_3C\text{—}OH} \xrightarrow[573\ K]{Cu} \underset{\text{2-Methyl propene}}{CH_3\text{—}C(CH_3){=}CH_2} + H_2O$$

(*iii*) **Esterification :** Alcohols react with organic acids to form esters in the presence of dehydrating agents such as sulphuric acid or dry hydrogen chloride. This process is reversible. By using one of the reactants in excess or by removing water, the reaction proceeds in forward direction.

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \quad \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Since the carboxylic acids themselves are not very reactive, these are first converted to acid chlorides or acid anhydrides and then are made to react with alcohol in the presence of pyridine (to absorb the acid formed). It results in the formation of ester. The process is known as **acylation.**

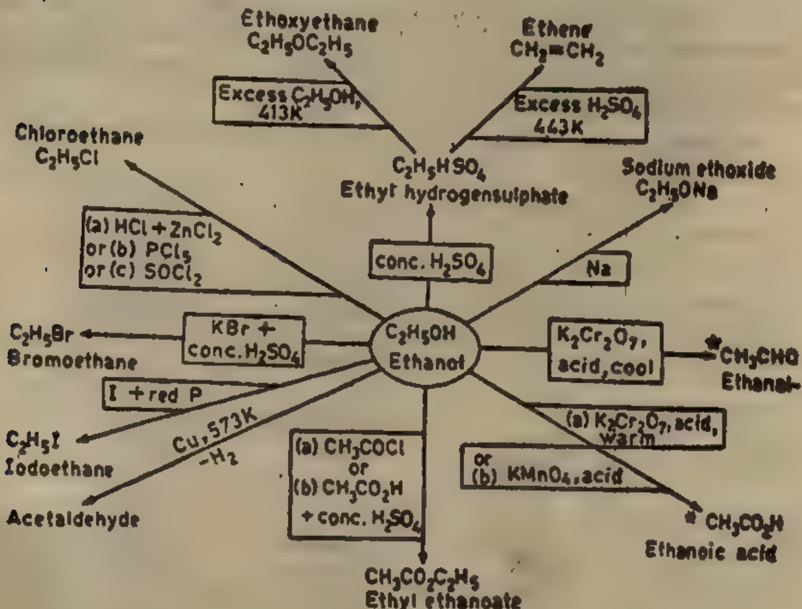
$$CH_3CO\boxed{Cl + H}OC_2H_5 \xrightarrow[-HCl]{\text{Pyridine}} CH_3COOC_2H_5$$

Acetyl chloride — Alcohol — Ethyl acetate

$$(CH_3CO)_2O + HOC_2H_5 \xrightarrow[-CH_3COOH]{\text{Pyridine}} CH_3COOC_2H_5$$

Acetic anhydride — Ethyl acetate

Some important reactions of ethanol are summarized in Fig. 7.7.



*Secondary alcohols are oxidised to ketones. Tertiary alcohols are more difficult to oxidize. With powerful, acidic oxidising agents, they form a mixture of acids.

Fig. 7.7. Reactions of ethanol.

Methods of Distinguishing Alcohols

(*i*) **Lucas test** : This test is based on the difference in reactivity of the three classes of alcohols towards the Lucas reagent (a mixture of concentrated hydrochloric acid and anhydrous zinc chloride). The reagent reacts with alcohols to form the corresponding insoluble alkyl chlorides with different speeds. Tertiary alcohols

react immediately to give a cloudiness due to the formation of the chloride. With secondary alcohols, the cloudiness appears after a few minutes while with primary alcohols no appreciable reaction is observed at room temperature.

(*ii*) **Oxidation with $K_2Cr_2O_7$ or $KMnO_4$** : Primary alcohols are first oxidized to aldehydesand then to carboxylic acids containing the same number of carbon atoms, as the original alcohols.

Secondary alcohols are oxidized to ketones, with the same number of carbon atom as the original alcohols. The ketone on further drastic oxidation gives an acid with a lesser number of carbon atoms than the original alcohol.

Tertiary alcohols do not undergo any oxidation in neutral or alkaline medium. With acid oxidizing agents, it gives a mixture of ketone and carboxylic acid each containing a lesser number of carbon atoms than the original alcohol.

Methods of distinguishing between primary, secondary and tertiary alcohols

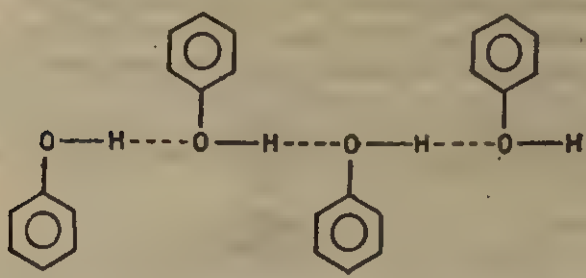
Reagent	*Primary alcohol*	*Secondary alcohol*	*Tertiary alcohol*
Acidified $K_2Cr_2O_7$ (orange)	Aldehyde, RCHO formed [blue Cr^{3+} (aq) formed]	Ketone, R_2CO formed (blue Cr^{3+} (aq) formed)	Resists oxidation
Conc. H_2SO_4	Alkene formed slowly	Intermediate in speed	Alkene formed fast
Lucas reagent (Conc. HCl $+ZnCl_2$) Add to alcohol and place in boiling water bath.	Cloudiness due to formation of RCl is slow to appear, (Anhydrous conditions are needed for primary alcohols.)	Cloudiness appears in 5 minutes due to the formation of RCl	Cloudiness appears in 1 minute owing to the formation of RCl, which is insoluble in water.

7.7.7. Properties and Reactions of Phenols

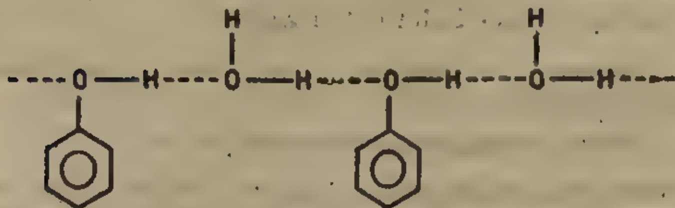
Simple phenols are liquids or low melting solids. They are usually crystalline solids at room temperature. They are colourless when pure but as usually seen they are red coloured owing to the presence of oxidation products. Boiling and melting points are

considerably higher than those of aliphatic alcohols and parent aromatic hydrocarbons (*e.g.*, phenol boils at 455 K and toluene at 384 K ; phenol melts at 315 K and toluene at 178 K) since phenols are not only associated by intermolecular hydrogen bonding but also by the attraction of polarised resonance structures.

Phenol itself and some di- and trihydric phenols are fairly soluble in water as they form hydrogen bonds with water much in the same fashion as do aliphatic alcohols. Some other phenols are insoluble in water because of the dominant hydrocarbon part in the molecule.



Intermolecular hydrogen bonding in phenol



Hydrogen bonding between phenol and water

Phenol is poisonous and caustic (*i.e.*, burns the skin).

Chemical properties : Phenols and alcohols differ significantly in their chemical reactions. This is attributed to structural difference between the two classes of compounds.

Phenols are very reactive compounds and their reactions can be divided into two classes :

1. those involving the phenolic —OH group, and
2. those involving the aromatic ring.

1. Reactions involving the phenolic —OH group

(*i*) **Acid character :** Phenols behave as weak acid because they ionize when dissolved in water to form phenoxide ion.

Phenol Phenoxide ion

Phenols are markedly more acidic than alcohols, although less so than carboxylic acids. They dissolve in aqueous sodium hydroxide to form soluble sodium salts known as phenoxide.

Phenol Sodium phenoxide

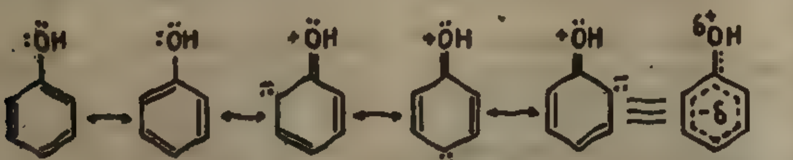
The introduction of nitro ($-NO_2$) and chloro groups increases the acidity of the phenols.

Acidity of phenol is due to two reasons :

(*i*) Resonance stabilisation of benzene ring by the non-bonded electron pair present on oxygen atom of the phenolic —OH.

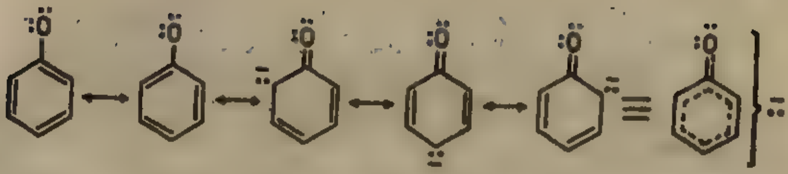
(*ii*) Resonance stabilisation of phenoxide ion.

Both phenol and phenoxide anion have three charged forms (III, IV and V) each with negative charge on the ortho and para position in addition to the two kekule forms (I and II). Charged forms of phenol do not help in stabilising the hybrid form because of charge separation.



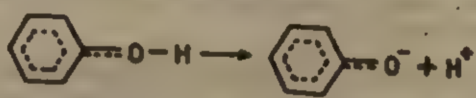
(I) (II) (III) (IV) (V) Resonance hybrid

Resonance forms of phenol

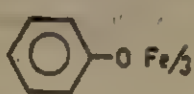


Resonance forms of phenoxide ion

However, there is no charge separation in the case of charged forms of phenoxide ions (III, IV and V). The charge is only delocalized. Thus, relatively the resonance hybrid of phenoxide ion is much more stable than the resonance hybrid of phenol itself. Thus, phenol residue becomes more stable after releasing H^+. This accounts for the acidic behaviour of phenols.



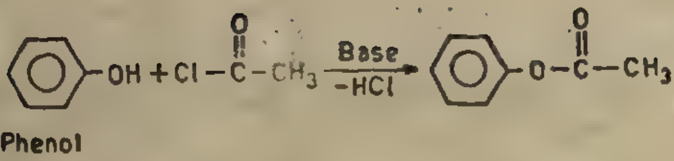
(*ii*) **Reaction with $FeCl_3$:** Phenols form coloured iron complexes with neutral $FeCl_3$. This reaction is often used as a test for phenols. Phenol gives violet colouration.



Iron complex

(*iii*) **Reaction with zinc dust :** When phenol is distilled with zinc dust the —OH group is replaced by H.

(*iv*) **Esterification :** Phenol forms esters with acyl halides or anhydrides in the presence of NaOH or pyridine.



This process is known as **acylation.**

Unlike alcohols, phenols are not directly esterified by reaction with a carboxylic acid.

Phenol reacts with ammonia forming aniline; reacts with PCl_5 forming aryl halides. Alkyl halides on reacting with phenoxide ion gives esters (Williamson synthesis, Unit 8).

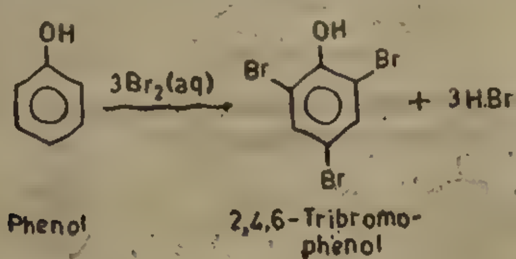
2. **Reactions involving the aromatic ring (substitution reactions)**

In these reactions, phenol behaves differently from alcohols due to the aromatic ring.

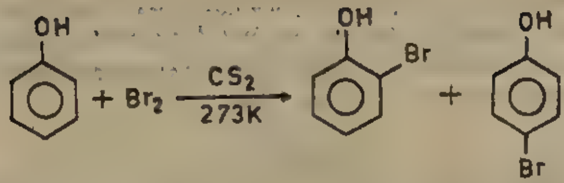
As mentioned earlier, the non-bonding electrons present on oxygen atom are shared by the ring. As a result of this, increase in electron density is seen in ortho and para positions.

Thus phenol undergoes electrophilic reactions and $-OH$ group directs them to ortho and para positions (activated positions).

(*i*) **Halogenation** : Phenol reacts with halogens to form polyhalogen substituted compounds. For example, phenol when treated with bromine water forms 2, 4, 6-tribromophenol (a white ppt.). The reaction is used in a quantitative method for the estimation of phenol.



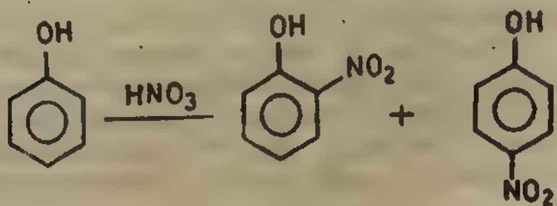
However, bromination may be limited to monoderivative by carrying out the reaction in less polar solvents at low temperature such as CCl_4, $CHCl_3$ or CS_2.



Phenol o-Bromo-phenol p-Bromo-phenol

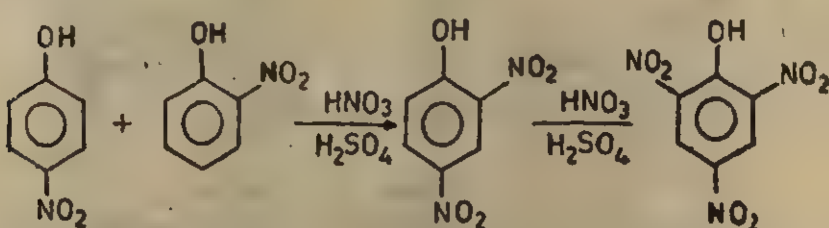
(*ii*) **Nitration** : Nitric acid is a strong oxidizing agent and direct nitration of phenol with dilute HNO_3 gives o- and p- nitro phenols in poor yield at room temperature (NO_2^+, nitronium ion is the electrophile).

$$HNO_3 + HNO_3 \longrightarrow NO_2^+ + NO_3^- + H_2O$$



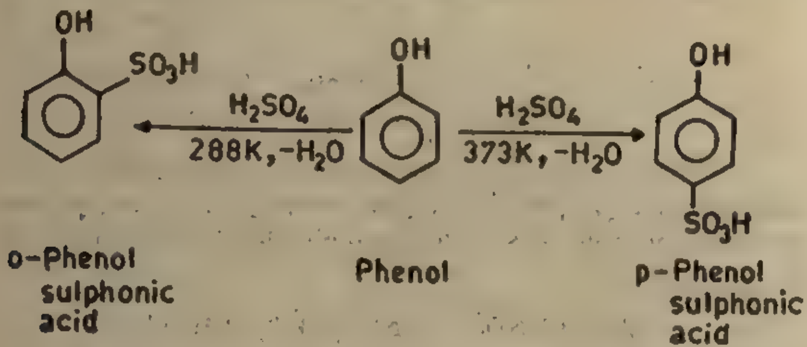
Phenol o-Nitro-phenol p-Nitro-phenol

Further nitration with nitrating mixture (conc. HNO_3+conc. H_2SO_4) gives first 2, 4-dinitrophenol and finally 2, 4, 6-trinitro phenol (picric acid). This compound is explosive when dry, and is stored under water.

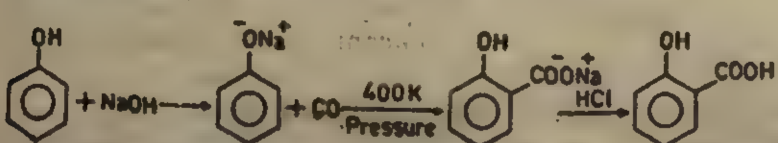


p-Nitro-phenol o-Nitro-phenol 2,4-Dinitro-phenol 2,4,6-Trinitro-phenol

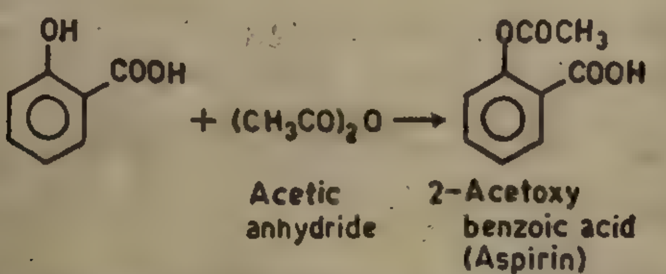
Sulphonation : Concentrated sulphuric acid sulphonates the phenol chiefly to ortho-isomer at low temperature and to para isomer at high temperature (SO_3, is the electrophile as it is an electron deficient group which later accepts H^+).



(*iii*) **Kolbe reaction :** The activating effect of the hydroxyl group in a phenol may be used to introduce 'groups' into the aromatic nucleus. Thus, sodium phenoxide (which is more active than phenol itself) on treating with CO_2 is converted to sodium solicylate which on acidifying with HCl yields 2-hydroxybenzoic acid (salicyclic acid). A small amount of p-hydroxybenzoic acid is also formed.

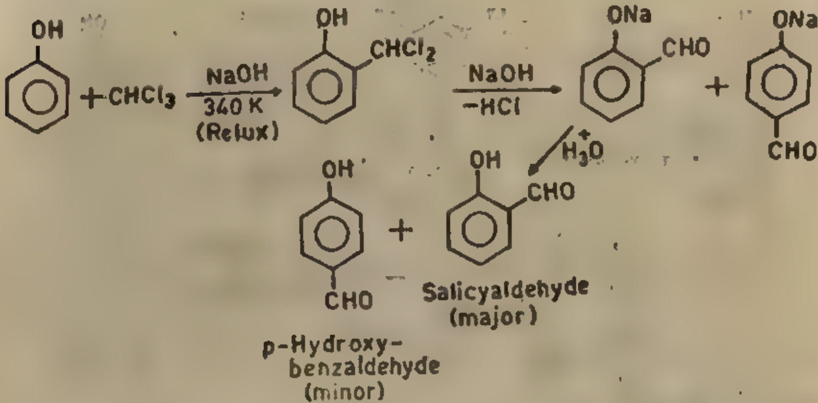


Salicyclic acid is used for manufacturing 2-acetoxybenzoic acid (aspirin).

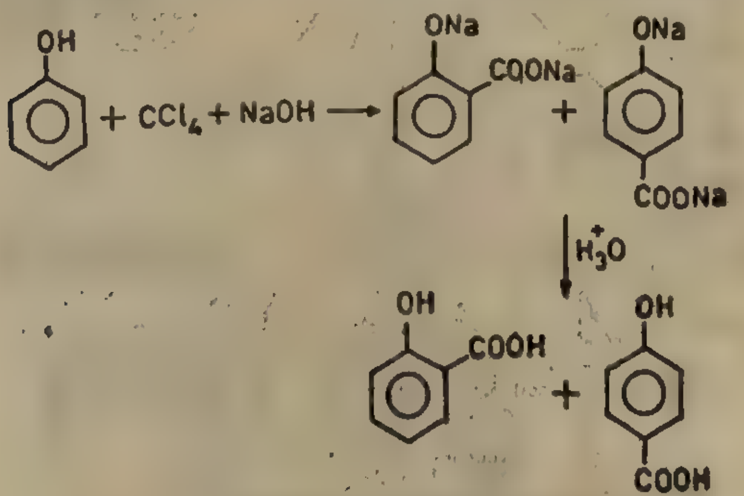


(*iv*) **Reimer-Tiemann reaction :** In this reaction, the activity of the phenoxide ion is used to introduce an aldehyde group into a

phenol. Thus, treatment of phenol in the presence of aqueous alkali with chloroform at 340 K, followed by hydrolysis of the resulting product gives a mixture o-hydroxy benzaldehyde (salicyaldehyde) and p-hydroxy benzaldehyde.



There is another Reimer-Tiemann reaction wherein on refluxing a solution of phenol in sodium hydroxide with carbon tetrachloride, a mixture of o-hydroxybenzoic acid and p-hydroxy benzoic acid is formed.



o-hydroxy-benzoic acid

p-hydroxy-benzoic acid

Methods of preparations and important reactions of phenol are summarized in Figs. 7.8. and 7.9.

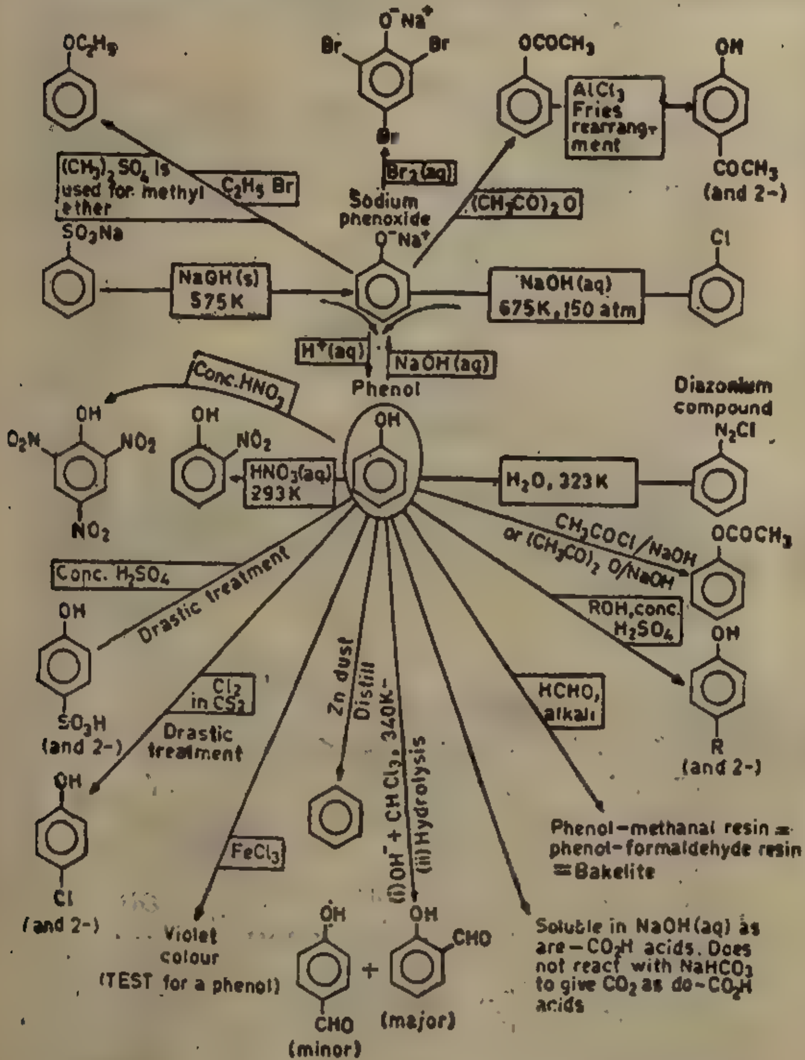
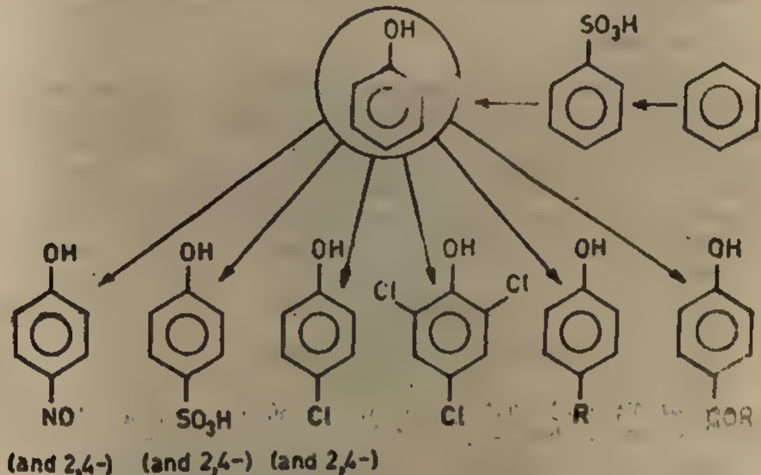


Fig. 7.8. Methods of preparation and reactions of phenol

(I) The —OH group directs other substituents into the ring.



Every one of the products of these reactions may be used as a starting point for all the reactions shown below.

(II) The —OH group is replaced by a different group.

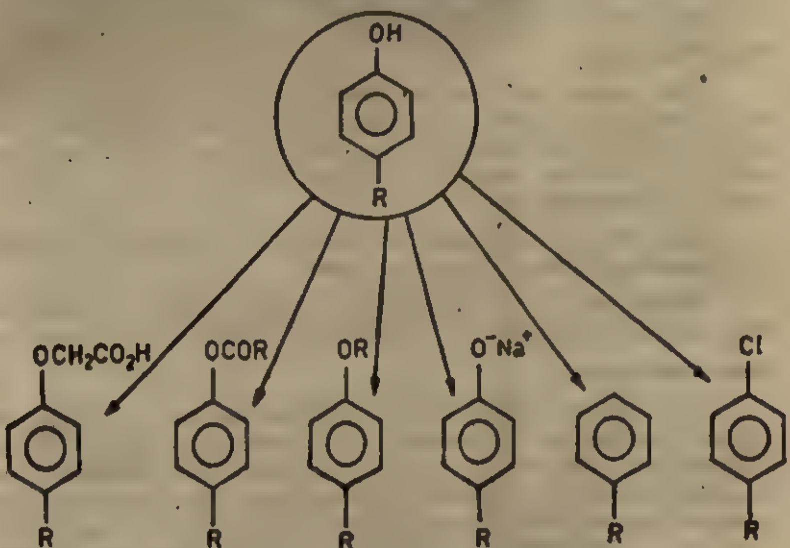


Fig. 7.9. Aromatic compounds from phenol.

7.8. COMMERCIALLY IMPORTANT ALCOHOLS AND PHENOLS

7.8.1. Methanol

At one time, most methanol was produced by the destructive distillation of wood (*i.e.*, heating wood at high temperature in the absence of air). It was because of this method of production, that methanol came to be called "wood alcohol". Today, most of the methanol is produced by the catalytic hydrogenation of carbon monoxide. A mixture of carbon monoxide and hydrogen is passed over a catalyst. This reaction takes place under high pressure and at a temperature of 573 to 673 K.

$$CO + 2H_2 \xrightarrow[200-300 \text{ atm}]{ZnO-Cr_2O_3,\ 573-673\text{ K}} CH_3OH$$

An excess of hydrogen is used in this reaction, and any unreacted CO is removed by dissolution in copper (I) methanoate solution.

Methanol is a colourless liquid with bp 337 K. It is highly toxic. Ingestion of even small quantities of methanol can cause blindness ; large quantities cause death. Methanol poisoning can occur even by inhalation of the vapours or by prolonged exposure of the skin. It is used for the production formaldehyde (methanal) which is used in the manufacture of plastics. It is used as a solvent for paints, varnishes, oils and polishes.

7.8.2. Ethanol

Ethyl alcohol has been produced throughout the centuries by the fermentation of starches and sugars, and it is the alcohol of all alcoholic beverages. Ethanol produced by fermentation is used in industry but more especially for consumption in the form of beer, wines and spirits.

Most of the ethanol used for industrial purposes is produced by the acid-catalyzed hydration of ethene.

Industrial alcohol is 95% ethyl alcohol. It forms an azeotrope with water. This mixture is sold as rectified spirit.

Absolute alcohol

By fractional distillation of a dilute aqueous solution of alcohol (as obtained, for example, from fermentation) the maximum concentration that can be obtained is about 95% ethanol called **rectified spirit.** In order to get pure alcohol, also called **absolute alcohol,** rectified spirit is mixed with some benzene and fractionally distilled. Three fractions are obtained. The first fraction, obtained at 337 K, is a constant boiling mixture containing benzene, water and ethanol. After all the water has been removed in this mixture a second fraction of benzene and ethanol is obtained (bp 341 K).

After all the benzene has been removed in this fraction then pure ethanol distils over at 351K.

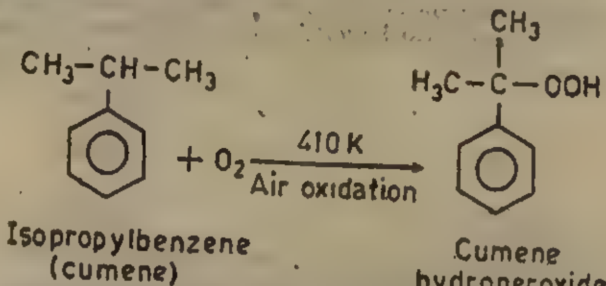
Alcohol in industry

Ethanol is an important industrial solvent. Since alcohol, meant for use as a solvent, may be used for drinking. Government regulations require that it be marketed after making it unfit for drinking purposes. This is done by addition of methanol and the product is called **methylated spirit** or denatured alcohol. Alcohol has been found to be a good fuel and alcohol-petrol mixtures have been tried as fuel for automobiles. When used as a fuel it is referred to as **power alcohol.**

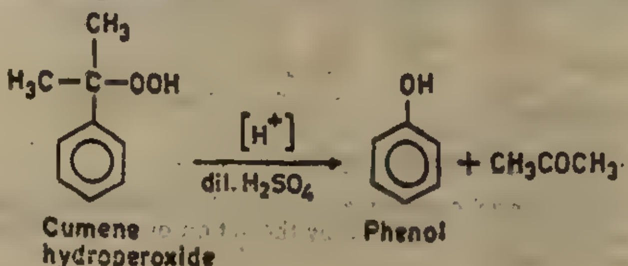
Ethanol is a colourless liquid with b.p. 351K. It is a hypnotic (sleep producer). It depresses activity in the upper brain even though it gives the illusion of being a stimulant. It is toxic in nature, but it is much less toxic than methyl alcohol. It is widely used for the manufacture of other chemicals including ethanol, ethanoic acid and esters, etc.

7.8.3. Phenol

Phenol is produced commercially from cumene (2-phenyl propane). Cumene is taken in a solution of dilute sodium carbonate. Air or oxygen is passed through the solution at 410K when cumene hydroperoxide is obtained.

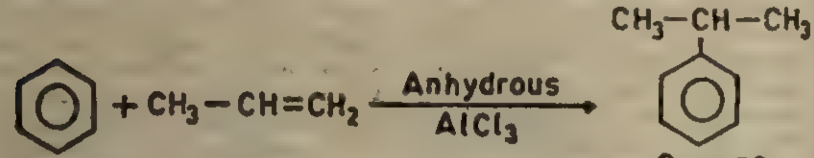


The hydroperoxide is boiled with dilute H_2SO_4 (10%), when a molecular rearrangement takes place resulting into the production of acetone and phenol.



Acetone is separated from phenol by distillation.

Cumene for the purpose can be obtained by treating benzene with propylene in the presence of anhydrous aluminium chloride, (Friedel-Crafts reaction).



Benzene Propylene Cumene (Isopropylbenzene)

This is the most recent commercial synthetic method of phenol. This method is assuming great importance as a useful commercial chemical acetone is obtained as a by-product.

Phenol is widely used as a disinfectant. It is used in the plastics industry by way of phenol-formaldehyde resins. It is also used in the production of dyes, explosives, insecticides. It was the first antiseptic in use.

7.8.4. Polyhydric alcohols

Polyhydric alcohols contain two or more alcoholic groups in their molecules. Two most important polyhydric alcohols are—ethylene glycol and glycerol.

$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \qquad\qquad \begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Ethylene glycol (a dihydric alcohol) — Glycerol (a trihydric alcohol)

In polyhydric alcohols, more than one hydroxyl group cannot remain attached to the same carbon atom because this gives rise to an unstable arrangement. Such an arrangement undergoes a spontaneous change and loses a molecule of water. For example,

$$CH_3CH\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} \xrightarrow{-H_2O} CH_3CHO$$

(Unstable arrangement)

(I) 2-Ethane diol (ethylene glycol)

Ethylene glycol commonly called glycol is the most important dihydric alcohol. It is prepared by the action of alkaline $KMnO_4$ or osmium tetraoxide.

$$3\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2KMnO_4 + 4H_2O \xrightarrow{\text{Cold}} 3\begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array} + 2\,MnO_2 + 2KOH$$

Ethylene glycol

It is necessary to use mild conditions as otherwise permanganate being a strong oxidizing agent, may oxidize the glycol further.

It is manufactured by the hydrolysis of ethylene oxide. Ethylene oxide (also called ethylenepoxide) is prepared by oxidation of ethylene with air in presence of a silver catalyst at 475-675K, under pressure. This is hydrolyzed by dil. acid :

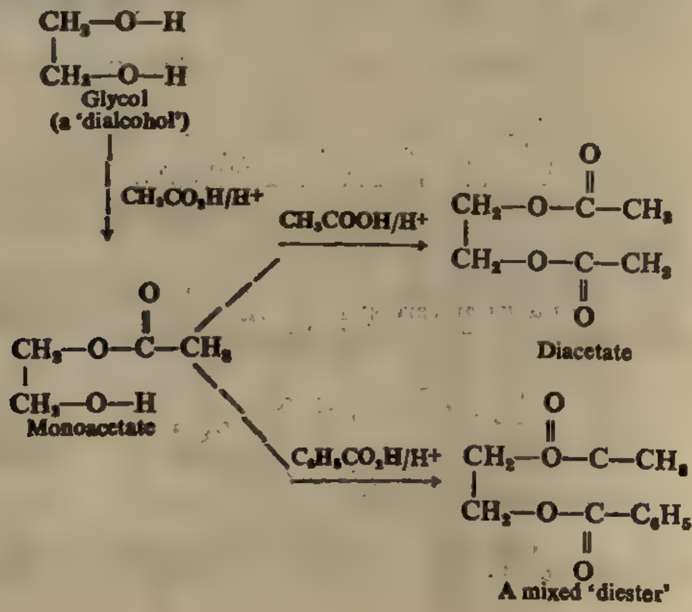
$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + \tfrac{1}{2}O_2 \xrightarrow[475\text{-}675K]{\text{Ag catalyst}} \underset{\text{Ethylene oxide}}{\begin{array}{c}CH_2\\ |\\ CH_2\end{array}\!\!>O} \xrightarrow[\text{dil. HCl}]{H_2O} \underset{\text{Ethylene glycol}}{\begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}}$$

Properties and chemical reactions

Glycol is a colourless syrupy liquid with a high boiling point of 470K. The high boiling point is due to the large degree of hydrogen bonding arising from the presence of two hydroxyl groups. Again, due to hydrogen bonding, it is highly soluble in water and ethanol, but is insoluble in ether.

It is a poisonous liquid.

There are two primary alcoholic groups present, one or both may react. Thus, two series of esters, ethers, halides *etc.*, can be formed from the diol :

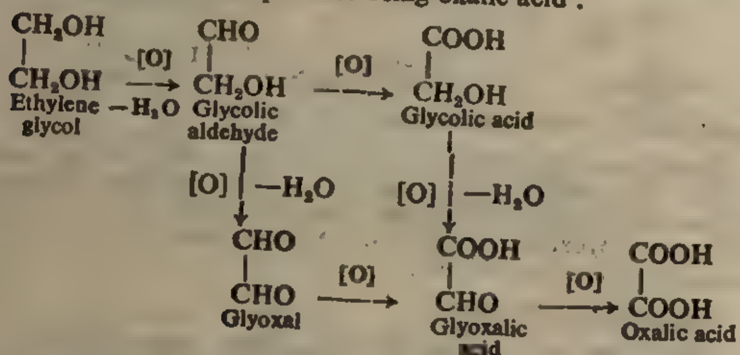


In addition to these reactions, glycol gives certain characteristic reactions like oxidation, dehydration (pinacole-pinacolone rearrangement), *etc.*

Oxidation. Monohydric primary alcohols may be oxidized first to alcohols and then to acids :

$$R-CH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-CO_2H$$

Ethylene glycol on oxidation gives different products depending on the nature of oxidizing agent, temperature, *etc.* When oxidized with nitric acid, it forms a series of products depending upon the sequence and extent of oxidation of the two—CH_2—OH groups present in it, the final product being oxalic acid :



On oxidation with periodic acid or lead tetracetate, the cleavage of carbon-carbon bond occurs with the formation of formaldehyde.

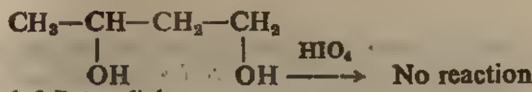
$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{or } Pb(OCOCH_3)_4]{HIO_4} \begin{array}{c} CH_2{=}O \\ + \\ CH_2{=}O \end{array}$$

This oxidative cleavage is very useful in determination of the structure of the parent vicinal glycol since no two different glycols give the same combination of products.

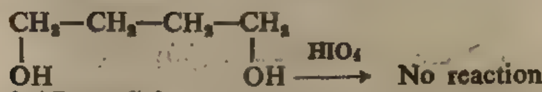
The identification of these carbonyl compounds, indicates the position of adjacent carbon atoms carrying the two hydroxyl groups. Thus, the various butane-diols react as follows :

$$\underset{\text{1, 2-Butanediol}}{\begin{array}{l} CH_2{-}CH{-}CH_2{-}CH_3 \\ \;|\quad\;\;| \\ OH\;\;OH \end{array}} \xrightarrow{HIO_4} \underset{\text{Formaldehyde}}{HCHO} + \underset{\text{Propionaldehyde}}{CH_3CH_2CHO}$$

$$\underset{\text{2, 3-Butanediol}}{\begin{array}{l} CH_3{-}CH{-}CH{-}CH_3 \\ \qquad|\quad\;\;| \\ \quad\;OH\;\;OH \end{array}} \xrightarrow{HIO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Acetaldehyde}}{CH_3CHO}$$

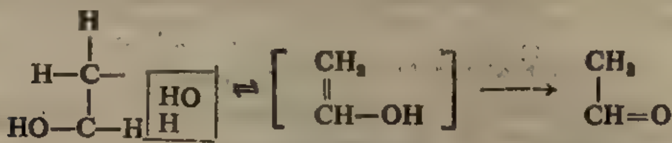


1, 3-Butanediol



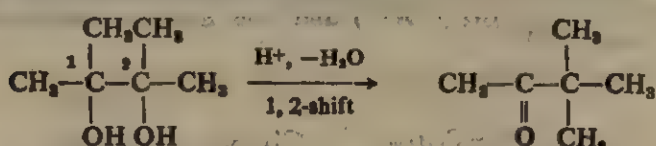
1, 4-Butanediol

Dehydration. (*i*) With dehydrating agents like sulphuric acid, glycol dehydrates and the product rearranges to form acetaldehyde.



Vinyl alcohol (unstable) Acetaldehyde

(*ii*) Higher vicinal-diols undergo acid-catalyzed dehydration followed by rearrangement. Thus, pinacol (tetramethyl glycol) in presence of acid, is dehydrated and undergoes rearrangement to form pinacolone (a ketone). This reaction, called the pinacol-pinacolone rearrangement, involves the migration of an alkyl group, from one carbon to an adjacent carbon and is an example of a class of rearrangements, called **1, 2-shifts**.



Pinacol* 2, 3-Dimethyl-2, 3-butanediol

Pinacolone 3, 3-Dimethyl-2-butanone

Uses of Ethylene Glycol

(*i*) It is used as an antifreeze for automobile radiators and as a coolant for aeroplane motors under the name **prestone**.

(*ii*) Its ethers like **cellosolve**, **carbitol** and **diglyme** are excellent solvents for oils, fats, waxes, lacquers, enamels, *etc*.

$$CH_3{-}CH_2{-}O{-}CH_2{-}CH_2{-}OH$$

Cellosolve

(Ethylene glycol monoethyl ether)

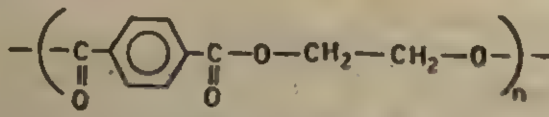
$$C_2H_5{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}OH$$

Carbitol

$$CH_3{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}OCH_3$$

Diglyme

(*iii*) Some esters of glycol are used in the manufacture of synthetic fibres. The well-known synthetic fibre **dacron** is a polyester of ethylene glycol with terephthalic acid.



Decron (or terylene)

(*iv*) Its dinitrate is used as an explosive along with glyceryl-trinitrate.

(II) 1, 2, 3-Propanetriol (glycerol or glycerine)

Glycerol commonly known as glycerine is the only important trihydric alcohol and has the structure :

$$\begin{array}{ccccc} CH_2 & - & CH & - & CH_2 \\ | & & | & & | \\ OH & & OH & & OH \end{array}$$

Glycerol
(Propane-1, 2, 3-triol)

It is present widely in natuse in vegetable oils and animal fats as glycerides—esters of glycerine and long chain fatty acids. Three acids are quite common two saturated, palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$) and one mono unsaturated, oleic acid ($C_{17}H_{33}COOH$) :

$$\begin{array}{l} CH_2-O-CO-C_{17}H_{35} \\ | \\ CH-O-CO-C_{17}H_{35} \\ | \\ CH_2-O-CO-C_{17}H_{35} \end{array} \qquad \begin{array}{l} CH_2-O-CO-C_{17}H_{33} \\ | \\ CH-O-CO-C_{17}H_{33} \\ | \\ CH_2-O-CO-C_{17}H_{33} \end{array}$$

Glyceryl tristearate (Tristearin) — **Glyceryltrioleate (Triolein)**

Glycerides having unsaturated acids have a lower melting point than saturated ones : Compare Tristearin, mp 344K with triolein, mp 290K.

Unsaturated fats (polyunsaturated preferable) are much more easily digested. You must have noticed the popularity of refined groundnut oil over vanaspati (saturated fats). Polyunsaturated oils are especially recommended for people prone to heart problems.

Glycerol is obtained both from natural glycerides and also synthetically :

Fats and oils on hydrolysis with alkali yield glycerol and a mixture of salts of fatty acids, called soaps.

$$
\begin{array}{llcll}
CH_2-O-\boxed{-COR_1+NaO}\,H & & CH_2OH & & R_1COONa \\
\;| & & \;| & & \;\;+ \\
CH-O-\boxed{COR_2+NaO}\,H & \longrightarrow & CHOH & + & R_2COONa \\
\;| & & \;| & & \;\;+ \\
CH_2-O-\boxed{COR_3+NaO}\,H & & CH_2OH & & R_3COONa \\
\text{Glyceride} & & \text{Glycerol} & & \text{(Salts of higher} \\
\text{(An oil or fat)} & & & & \text{fatty acids) Soap}
\end{array}
$$

R_1, R_2, R_3 are high molecular mass alkyl groups (C_{12} to C_{18}). The reaction is used for the manufacture of soap. Therefore, glycerol is obtained as a by-product of soap industry.

The 'soft soaps' are usually the potassium salts of higher fatty acids.

Glycerol can also be liberated from fats or oils by **transesterification** with methyl alcohol. Transesterification is catalyzed by acids (H_2SO_4 or dry HCl) or base (usually alkoxide ion, RO^-)

$$
\begin{array}{llll}
CH_2O-OCR' & & CH_2OH & R'COOCH_3 \\
\;| & & \;| & \;\;+ \\
CHO-OCR''+3CH_3OH & \rightarrow & CHOH & +R''COOCH_3 \\
\;| & & \;| & \;\;+ \\
CH_2O-OCR''' & & CH_2OH & R'''COOCH_3 \\
\text{Fat or oil} & & \text{Glycerol} & \text{Methyl esters of} \\
 & & & \text{fatty acids}
\end{array}
$$

Glycerol is also manufactured by hydration of propylene by a number of routes.

Properties and chemical reactions

Glycerol is a syrupy liquid.

It has a high bp (563K) due to strong hydrogen bonding.

Again, hydrogen bonding makes it soluble in water and ethanol in all proportions, but insoluble in ether.

It is sweet in taste and very hygroscopic (due to hydrogen bonding) in nature, and therefore, is useful as a moistening agent in shaving soap, *etc.*

Glycerol contains two primary and one secondary alcoholic groups and it gives all the usual reactions of these groups. In addition, it also undergoes some special reactions because of the presence of vichydroxyl groups. Some of the important reactions are :

(*i*) **Nitration** : The ester glyceryl trinitrate (commonly called nitroglycerine) is obtained when glycerol is added carefully to a mixture of concentrated nitric acid and sulphuric acid maintained at 283-298K.

It is necessary to use mild conditions to reduce the oxidation of glycerol itself by the nitrating mixture.

$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH+3HONO_2 \\ | \\ CH_2-OH \end{array} \qquad \begin{array}{l} CH_2-O-NO_2 \\ | \\ CH-O-NO_2 \\ | \\ CH_2-O-NO_2 \end{array} + 3H_2O$$

Nitroglycerine
(Glyceryl trinitrate)

(*ii*) **Ester formation** : Three moles of acid chloride react to form a triester, confirming the presence of three hydroxyl groups :

$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} \xrightarrow{3ROCl} \begin{array}{l} CH_2-O-COR \\ | \\ CH-O-COR \\ | \\ CH_2-O-COR \end{array} + 3HCl$$

(*iii*) **Action of HI** : Glycerol has three replaceable hydroxyl groups and would be expected to ultimately form, 1, 2, 3-triiodopropane with HI or PI_3 The actual products obtained are quite different and depend on the amount of reagent used.

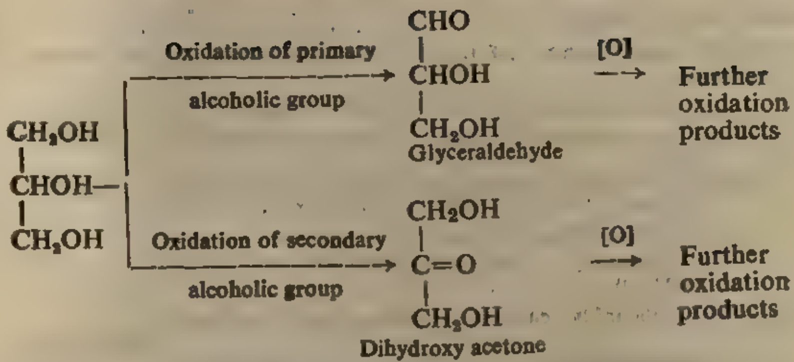
(*a*) With small amount of HI or PI_3, the main product formed is allyl iodide :

$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} \xrightarrow[PI_3]{HI\ or} \underset{\text{1, 2, 3-Triiodo-propane (unstable)}}{\begin{array}{l} CH_2-I \\ | \\ CH-I \\ | \\ CH_2-I \end{array}} \xrightarrow{-I_2} \underset{\text{Allyl iodide}}{\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2-I \end{array}}$$

(*b*) With excess phosphorus triiodide, allyl iodide first formed reacts further to yield isopropyl iodide as the main product :

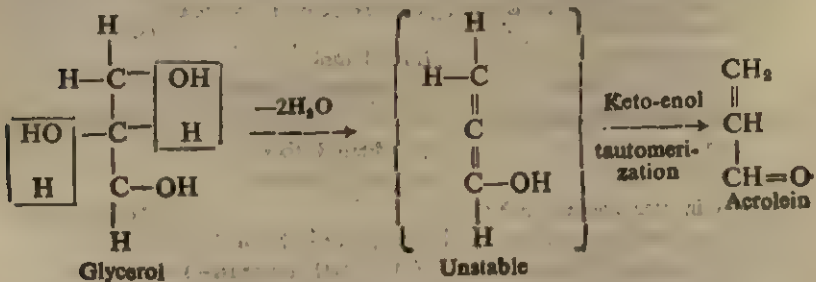
$$\underset{\text{Allyl iodide}}{\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array}} \xrightarrow{HI} \begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_2I \end{array} \xrightarrow{-I_2} \underset{\text{Propylene}}{\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array}} \xrightarrow{HI} \underset{\text{Isopropyl iodide}}{\begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_3 \end{array}}$$

(*iv*) **Oxidation** : Presence of two primary alcoholic and one secondary, makes a variety of oxidation products possible (using different oxidizing agents) :



Thus, a mild oxidizing agent, like Fenton's reagent (H_2O_2 $+FeSO_4$) gives a mixture of glyceraldehyde and dihydroxyacetone. Upon further oxidation these are oxidized to oxalic acid then to formic and finally to CO_2.

(*v*) **Dehydration.** When heated alone or with dehydrating agents (*e.g.*, $KHSO_4$) glycerol is first converted to an unstable enol which undergoes keto-enol tautomerization to the stable acrolein :



Glycerol is used : 1. In the manufacture of nitroglycerine*, important us an explosive and as a stimulant for the heart. 2. In the manufacture of medicines, cosmetics, shaving soap and translucent soaps. 3. In the manufacture of glyptal, a polyester of glycerol and phthalic acid. 4. In printing inks, copying inks, stamp pads, water colour pigments, textile processings. 5. As an antifreeze (*i.e.*, similar to glycol). 6. As a moistening agent for processed products like tobacco, leather goods, *etc.* 7. As a preservative and sweetening agent for foods.

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*An important explosive using nitroglycerine is dynamite :

Dynamite. Alfred Nobel (of 'Nobel prizes fame') a Swedish chemist, discovered that nitroglycerine, an explosive substance, could be stabilized for transportation by absorption on Kiesulguhr (a kind of earth). This was dynamite. However now it is manufactured by absorbing it in sawdust and some solid ammonium nitrate is also added.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

7·1 Choose the correct answer of the four alternatives given for the following questions :

(*i*) An industrial method of preparation of methanol is : (*I.I.T., 1984*)

(*a*) Catalytic reduction of carbon monoxide in presence of ZnO—Cr_2O_3,

(*b*) by reacting methane with steam at 900°C with a nickel catalyst,

(*c*) by reducing formaldehyde with $LiAlH_4$,

(*d*) bv reacting formaldehyde with aqueous sodium hydroxide solution.

(*ii*) When phenol is treated with excess bromine water, it gives : (*I.I.T., 1984*)

(*a*) m-bromophenol, (*b*) o- and p-bromophenol

(*c*) 2, 4-dibromophenol (*d*) 2, 4, 6 tribromophenol

(*iii*) Chlorobenzene can be prepared by reacting aniline with : (*I.I.T., 1984*)

(*a*) hydrochloric acid

(*b*) cuprous chloride

(*c*) chlorine in the presence of anhydrous aluminium chloride

(*d*) nitrous acid followed by heating with cuprous chloride.

(*iv*) The compound that will not give iodoform on treatment with alkali and iodine is (*I.I.T., 1985*)

(*a*) acetone (*b*) ethanol

(*c*) diethyl ketone (*d*) isopropyl alcohol

(*v*) An isomer of ethanol is (*I.I.T., 1986*)

(*a*) methanol (*b*) diethyl ether

(*c*) acetone (*d*) dimethyl ether

(*vi*) HBr reacts as fast with : (*I.I.T. 1986*)

(*a*) 2-methyl propan—2—ol (*b*) propan—1—ol

(*c*) propan—2—ol (*d*) 2-methyl propan—1—ol

(*vii*) The reaction of toluene with chlorine in presence of ferric chloride gives predominantly. (*I.I.T., 1986*)

(*a*) benzoyl chloride (*b*) m-chlorotoluene

(*c*) benzyl chloride (*d*) o- and p-chlorotoluence

(*viii*) Phenol is less acidic than : (*I.I.T., 1986*)

(*a*) acetic acid (*b*) p-methoxy phenol

(*c*) p-nitrophenol (*d*) ethanol

(*ix*) *n*-Propyl bromide on treatment with ethanolic potassium hydroxide produces : (*I.I.T., 1987*)

(*a*) propane (*b*) propene

(*c*) propyne (*d*) propanol

(*x*) In CH_3 CH_2 OH, the bond that undergoes heterolytic cleavage most readily is (*I.I.T., 1988*)

(*a*) C—C (*b*) C—O

(*c*) C—H (*d*) O—H

(*xi*) Phenol reacts with bromine in carbon disulphide at low temperature to give : (*I.I.T.*, *1988*)

(*a*) m-bromophenol (*b*) o- and p-bromophenols

(*c*) p-bromophenol (*d*) 2, 4, 6 –tribromophehol

(*xii*) Chloroform is obtained from C_2H_5OH by treating it with

(*a*) PCl_5 (*b*) $POCl_3$

(*c*) HCl (*d*) $CaOCl_2$

(*xiii*) Which of the following alkyl halides when subjected to dehydro halogenation by the action of ethanolic KOH would yield :

$$CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$$

(*a*) $CH_3-CH\ (Br)\ CH\ (CH_3)_2$

(*b*) $CH_3\ CH_2\ CH\ (CH_3)-CH_2\ Br$

(*c*) $CH_3\ CH_2\ CH_2\ Br\ CH_2\ CH_3$

(*d*) $CH_3\ CH\ Br\ (CH_2)_2\ CH_3$

(*xiv*) The Sandmeyer reaction of diazonium salts is a elimination reaction of N_2 by

(*a*) halides (*b*) hydroxyl group

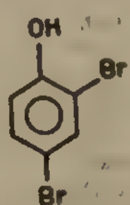
(*c*) hydrogen (*d*) nitro group.

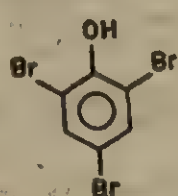
(*xv*) Which of the following species is not found in the mechanism of the peroxide (ROOR) catalyzed addition of HBr to propene ?

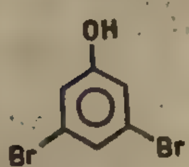
(*a*) $R-\underset{\cdot\cdot}{\ddot{O}}:$ (*b*) CH_3-CH_2-CH-H

(*c*) $:\underset{\cdot\cdot}{\ddot{Br}}\cdot$ (*d*) $R-OH$

(*xvi*) Phenol on reacting with excess aqueous bromine at room temperature gives

(a) 

(b) 

(c) 

(d) 

7.2 State if the following statements are true or false by writing T or F against each statement :

(*i*) HCl reacts with primary alcohol to produce corresponding alkyl chloride.

(ii) Carbon tetrachloride is a polar molecule.

(iii) 1, 2—Dichloroethane on reaction with chlorine forms only one trichloroethane.

(iv) Halogenation of the alkanes is an oxidation reaction.

(v) The ease of de hydration of alcohols takes place as suggested ; primary >secondary>tertiary.

(vi) Aliphatic alcohols act as a base as they can accept a proton to give a protonated product, *e.g.* $C_2H_5O^+H_2$.

(vii) All the ortho-and para-directing groups activate the benzene ring.

(viii) Electrophiles are Lewis acids.

(ix) Electron withdrawing groups attached to benzene ring make phenols more acidic than phenol (C_6H_5OH)

(x) It is easy to oxidize ethanol than phenol.

7·3 Fill in the blanks with appropriate words :

(i) A nucleophile is a reagent that can.........electrons to other species.

(ii) The elimination of.........from a haloalkane is called dehydrohalogenation.

(iii) The addition of HBr in the presence of peroxides to unsymmetrical alkenes takes place contrary to.........

(iv) The reactivity of alcohols in their reactions with hydrogen halides is in the order.........

(v) The melting and boiling points of haloalkanes are generally.........than the parent alkanes.

(vi) Haloarenes are.........reactive than haloalkanes due to their.........

(vii) ....attack haloalkanes at the carbon atom to which the halogen atom is attached.

(viii) Haloalkanes form alkyl magnesium halides when treated with magnesium in.........as solvent. These products are called.........

(ix) Haloarenes undergo.........substitution reactions due to the presence of.........benzene ring.

(x) Aldehydes and ketones are reduced to.........alcohols, respectively.

(xi) Diazonium salts on steam distillation give.........

(xii) Reaction of phenol with conc. H_2SO_4 followed by conc. HNO_3 gives.........

7·4 Match the entries given in Columns A and B :

Column A	Column B
(i) BF_3	1. Alcohol $\xrightarrow{\text{Red P/Br}_2}$ Alkyl bromide
(ii) Reimer-Tiemann reaction	2. Insecticide
(iii) Kolbe reaction	3. Friedel Crafts reaction
(iv) Cumene	4. Pesticide
(v) Sandmeyer's reaction	5. $C_6H_5OH \xrightarrow{CHCl_3/NaOH}$ salicylaldehyde
(vi) Rosenmund reaction	6. Lewis acid
(vii) Dehydro halogenation	7. $CH_3-(CH_2)_2Br \xrightarrow[C_2H_5OH]{KOH} CH_3-CH=CH_2$
(viii) DDT	8. $C_6H_5OH \xrightarrow{NaOH/CO_2}$ Salicylic acid
(ix) BHC	9. Alkene+water gas $\xrightarrow[(ii)\ H_2/Ni]{(i)\ Co(CO)_4}$ Alcohol
(x) Oxo process	10. $C_6H_5NH_2 \xrightarrow[(ii)\ Cu_2Cl_2]{(i)\ NaNO_2/HCl} C_6H_5Cl$

Short Answer Questions

7.5 Write IUPAC names of the following compounds :

(*i*) $CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_2-Br$

(*ii*) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-CH_3$

(*iii*) $CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_2-Cl$

(*iv*) $CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_2-OH$

(*v*) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-Cl$

7.6 How are the following conversions effected ?

(*i*) 1-Propanol into 1-bromopropane
(*ii*) 1-Butane into 1-chloro butane
(*iii*) Benzene to bromobenzene
(*iv*) 1-Chloropropane to 1-propanol
(*v*) 2-Methyl 1-pentene to 2-methyl-2-pentanol
(*vi*) Ethene to ethnol
(*vii*) 1-Iodopropane to propene
(*viii*) Bromomethane to methyl magnesium bromide
(*ix*) Chlorobenzene to phenol
(*x*) Phenol to phenyl ethanoate

7.7 Give the names of the chief products obtained when bromoethane reacts with

(*i*) an aqueous alkali
(*ii*) sodium metal in dry ether
(*iii*) an alcoholic potassium hydroxide solution
(*iv*) magnesium followed by ethanol
(*v*) aminoethane

7.8 Explain the terms : nucleophilic and electrophilic substitutions.

7.9 (*a*) Arrange the following in order of increasing boiling points :

(*i*) $CH_3-CH_2-CH_2-CH_2-Br$
(*ii*) $CH_3-CH_2-CH_2-CH_2-OH$
(*iii*) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-OH$
(*iv*) $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$

(*b*) Explain the acidic character of phenol ?
(*c*) How is ethanol distinguished from phenol ?

TERMINAL QUESTIONS

7.1. Give the general methods of preparation of alkyl halides and aryl halides.

7.2. What are aryl halides ? How do they differ from alkyl halides ? Suggest methods for the preparation of halobenzenes.

7.3. Write short notes on (*a*) Grignard reagent, (*b*) Wurtz reaction, (*c*) Nomenclature, (*d*) Tautomerism.

7.4. How will you convert benzene into chlorobenzene ?
How does chlorobenzene react with the following : (*i*) NaOH, (*ii*) Mg in diethylether, (*iii*) NH_3 ?

7.5. Give IUPAC names of the following compounds :

(*i*) $CH_3\,CH_2\,CH_2Cl$

(*ii*) $CH_3\,CH_2\,\underset{\displaystyle Cl}{\underset{|}{CH}}\,CH_3$

(*iii*) $\underset{\displaystyle Cl}{\underset{|}{CH_2}}\,\underset{\displaystyle Cl}{\underset{|}{CH}}\,CH_3$

(*iv*) $\underset{\displaystyle Cl}{\underset{|}{CH_2}}\,CH_2\,\underset{\displaystyle Cl}{\underset{|}{CH_2}}$

(*v*) $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\Big\rangle CH{-}Br$

(*vi*) $CH_3\,CH_2\,CH\Big\langle\begin{matrix} Br \\ Br \end{matrix}$

7.6. (*a*) What are alkyl halides ? Give one example of each mono-, di-, tri- and tetrahalogen derivatives for ethane.

(*b*) Distinguish between primary, secondary and tertiary alkyl halides. Give one example in each case.

7.7. Give two methods for the preparation of ethyl iodide. Starting from C_2H_5Br how will you prepare (*i*) ethyl nitrile (*ii*) ethylamine, (*iii*) ethyl methyl ether, (*iv*) ethane, and (*v*) propionic acid.

7.8. (*a*) What are polyhalogen compounds ?

(*b*) Suggest a method for the preparation of chloroform from (*i*) ethyl alcohol, and (*ii*) acetone.

(*c*) What is the product obtained from chloroform when : (*i*) boiled with aqueous potassium hydroxide, (*ii*) is exposed to air and light, (*iii*) heated with silver powder.

7.9. (*a*) Name five importact halogen compounds with their applications.
(*b*) Discuss the synthetic importance of alkyl halides.

7.10. (*a*) What are haloforms ? Outline one method for their preparation.
(*b*) What is the iodoform test ?

7.11. What do you understand by (*i*) nucleophilic substitution, and (*ii*) electrophilic substitution. Give three examples of each.

7.12. How can n-butyl bromide be converted into : (*i*) n-octane, (*ii*) 1-hexane, (*iii*) n-butane, (*iv*) 1, 2-dibromobutane, (*v*) n-butylcyanide, and (*vi*) n-butylamine.

7.13. How can isopropyl chloride (2-chloropropane) be converted into : (*i*) isopropanol, (*ii*) propylene, (*iii*) 2-aminopropane, (*iv*) 2, 3-dimethylbutane, and (*v*) isopropylethyl ether.

7.14. Comment on the following : (*i*) alkyl halides get hydrolyzed easily, (*ii*) aryl halides are less reactive, and (*iii*) it is easier to replace a halogen atom by a hydroxyl group from ethyl chloride than chlorobenzene.

7.15. Rearrange the following :

(*i*) in order of increasing reactivities : RBr, RCl and RI.

(*ii*) in order of increasing ease of dehalogenation : primary halide, secondary halide and tertiary halide.

7.16. Suggest one chemical test to distinguish between :

(*i*) CH_3 Br and C_2C_5 Cl

(*ii*) C_2H_5 Br and C_6H_5 Br

(*iii*) C_6H_5 Cl and C_6H_5 CH_2 Cl.

7.17. (*a*) Define and explain Markovnikov's rule.

(*b*) What is peroxide effect ?

7.18. (*a*) How are alcohols obtained from aldehydes and ketones ?

(*b*) What are the industrial methods of obtainirg ethanol ? Give its uses.

7.19. (*a*) How is phenol obtained industrially ? Mention its uses ?

(*b*) What happens when phenol is (*i*) nitrated, and (*ii*) halogenated ?

7.20. What are Kolbe reactions ?

7.21. What do you understand by the following terms :

(i) Absolute alcohol, (*ii*) Power alcohol, and (*iii*) Denatured alcohol.

7.22. Give two examples of the following types af reactions seen in alcohols :

(*a*) Involving cleavage of oxygen hydrogen bond.

(*b*) Involving cleavage of carbon oxygen bond.

7.23. Explain giving reasons : (*i*) boiling point of an alkyl halide is higher than that of the corresponding alkane, (*ii*) alcohols have higher boiling points than haloalkanes of the same molecular mass, and (*iii*) phenols are more acidic than alcohols.

7.24. (*a*) Structurally, what is the difference between an alcohol and a phenol.

(*b*) How can the following be distinguished from each other : (*i*) primary, secondary and tertiary alcohols, (*ii*) phenol from ethanol, and (*iii*) benzyl alcohol from phenol.

7.25. (*a*) Give the reactions for the preparation of primary, secondary and tertiary alcohols from Gnignard reagent.

(*b*) What happens when a mixture of primary, secondary, and tertiary alcohols: (*i*) is oxidized using alkaline potassium permanganate, and

(*b*) is passed over heated copper (570 K).

7.26. (*a*) How can phenol be prepared from (*i*) benzene sulphonic acid, and (*ii*) chlorobenzene.

(*b*) Why do phenols undergo substitution reactions readily ? Explain.

7.27. What are glycerides ? How is glycerol obtained on a commercial scale ?

7.28. What is glycol ? How is it prepared ? Give its important properties and uses.

ANSWERS TO SELF ASSESSMENT QUESTIONS

7.1.

(*i*)	(*a*)	(*ii*)	(*d*)	(*iii*)	(*d*)	(*iv*)	(*c*)
(*v*)	(*d*)	(*vi*)	(*a*)	(*vii*)	(*d*)	(*viii*)	(*a*) and (*c*)
(*ix*)	(*b*)	(*x*)	(*d*)	(*xi*)	(*b*)	(*xii*)	(*d*)
(*xiii*)	(*a*)	(*xiv*)	(*a*)	(*xv*)	(*b*)	(*xvi*)	(*b*)

7.2.

(*i*)	*F*	(*ii*)	*F*	(*iii*)	*T*	(*iv*)	*T*	(*v*)	*F*
(*vi*)	*T*	(*vii*)	*F*	(*viii*)	*T*	(*ix*)	*T*	(*x*)	*T*

7.3. (*i*) donate
(*ii*) hydrogen halide
(*iii*) Markovnikov's rule
(*iv*) tertiary>secondary>primary
(*v*) higher
(*vi*) less, resonance stabilization
(*vii*) nucleophiles
(*viii*) dry ether, Grignard reagent
(*ix*) electrophilic, electron rich
(*x*) primary and secondary
(*xi*) phenols
(*xii*) 2, 4, 6-trinitrophenol.

7.4.

(*i*)	6.	(*ii*)	5.	(*iii*)	8.	(*iv*)	3.	(*v*)	10.
(*vi*)	1.	(*vii*)	7.	(*viii*)	2.	(*ix*)	4.	(*x*)	9.

7.5. (*i*) 1, 3-Dibromobutane
(*ii*) 2-Hydroxy-4-methyloctane
(*iii*) 2, 3-Dibromo-1-chloro-3-methylpentane
(*iv*) 1, 2, 3-Butanetriol
(*v*) 1-Chloro-2-propanol.

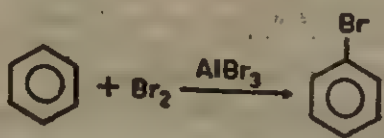
7.6. (*i*) 1-Propanol into 1-bromopropane

$$CH_3CH_2CH_2OH \xrightarrow[ZnCl_2]{HBr} \underset{\text{1-Bromo propane}}{CH_3CH_2CH_2Br}$$

(*ii*) 1-Butane into 1-chlorobutane

$$CH_3CH_2CH_2CH_3 \xrightarrow[-HCl]{Cl_2} \underset{\text{1-Chlorobutane}}{CH_3CH_2CH_2CH_2Cl}$$

(*iii*) Benzene to bromobenzene



(*iv*) 1-Chloropropane to 1-propanol

$$CH_3CH_2CH_2Cl + HOH \longrightarrow \underset{\text{1-Propanol}}{CH_3CH_2CH_2OH} + HCl$$

(v) 2-Methyl-1-pentene to 2-methyl-2-pentanol

$$\underset{\underset{CH_3}{|}}{CH_2=C}-CH_2-CH_2-CH_3 \xrightarrow{H_2SO_4} \underset{\underset{CH_3}{|}}{CH_3-C(HSO_4)}-\underset{\underset{\underset{CH_2}{|}}{CH_2}}{CH_2}$$

Boiling water ↓

$$\underset{\underset{CH_3}{|}}{CH_3-C(OH)}-CH_2-CH_2CH_3$$

2-hydroxy-2-methylpentane

(vi) Ethene to ethanol

$$\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{\text{Conc. } H_2SO_4} CH_3-CH_2-SOH_4 \xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

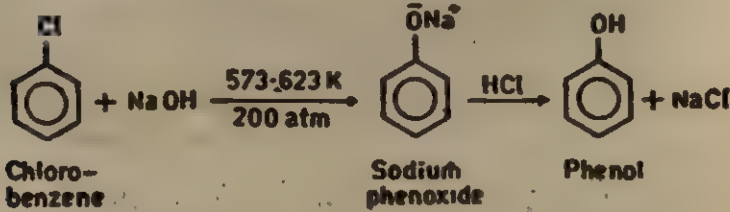
(vii) 1-Iodopropane to propene

$$CH_3CH_2-CH_2I \xrightarrow[-HI]{\text{Alcoholic KOH}} \underset{\text{Propene}}{CH_3CH=CH_2}$$

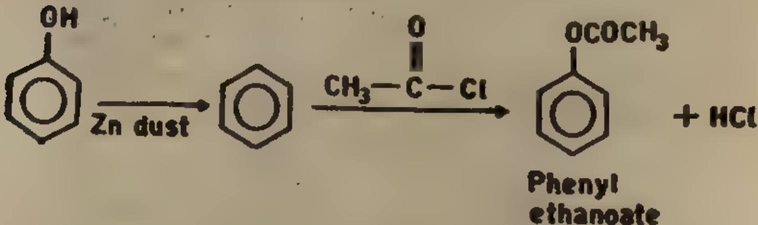
(viii) Bromomethane to methyl magnesium bromide

$$\underset{\text{Bromomethane}}{CH_3Br} \xrightarrow[\text{Ether}]{Mg} \underset{\text{Methyl magnesium bromide}}{CH_3MgBr}$$

(ix) Chlorobenzene to phenol



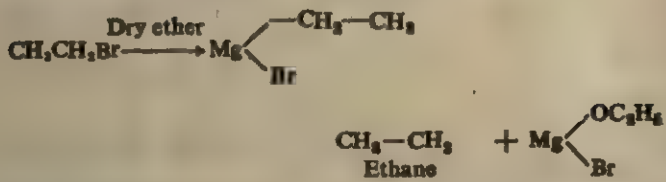
(x) Phenol to phenyl ethanoate



7.7. (i) $CH_3CH_2Br + KOH\ (aq) \longrightarrow \underset{\text{Methanol}}{CH_3CH_2OH}$

(ii) $2\ CH_3CH_2Br + 2Na \xrightarrow[\text{Ether}]{\text{Dry}} \underset{\text{Butane}}{CH_3CH_2-CH_2CH_3} + 2\ NaBr$

(iii) $CH_3CH_2Br \xrightarrow[-HBr]{KOH/C_2H_5OH} \underset{\text{Methanol}}{CH_3{-}CH_3}$

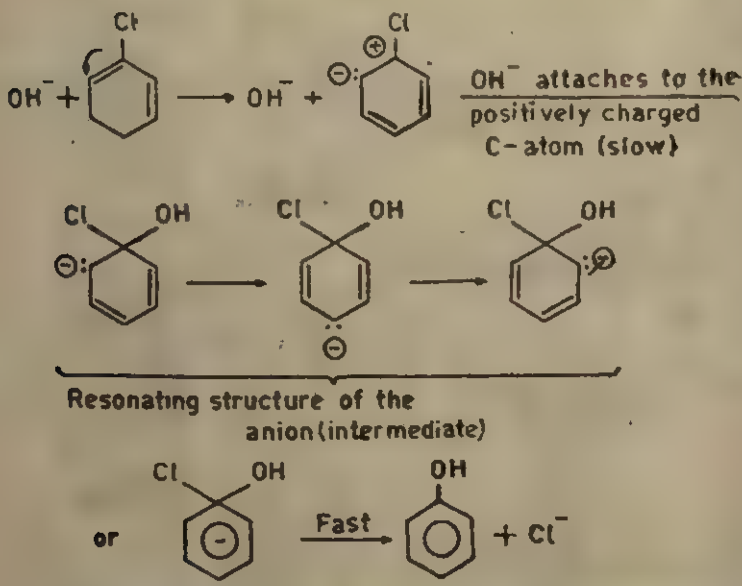
(iv) 

7.8. (i) **Nucleophilic substitution.** Replacement of hydrogen or any other substituent by a nucleophilic reagent is termed nucleophilic substitution. This substitution is mainly of two types—unimolecular ($S_N{}^1$) and bimolecular ($S_N{}^2$).

Unimolecular substitution. This mechanism is not common in aromatic substitution, Decomposition of aryldiazonium salt in aqueous solution to yield phenol or aryl halides exemplify this type of nucleophilic substitution.

$$\underset{\text{Aryl Diazonium salt}}{Ar-\overset{+}{N}{\equiv}N} \xrightarrow{\text{Slow}} N_2 + Ar^+ \xrightarrow[\text{Fast}]{H_2O} \underset{\text{Phenol}}{ArOH}$$

$$Ar^+ \xrightarrow[\text{Fast}]{Cl^-} \underset{\text{Aryl chloride}}{ArCl}$$



Bimolecular substitution. Nucleophilic substitutions in benzene ring are usually bimolecular. Preparation of phenol by the action of 10% NaOH solution on chlorobenzene under pressure at 575 K represents bimolecular nucleophilic substitution.

(*ii*) **Electrophilic substitution.** Electrophilic aromatic substitution proceeds by a bimolecular (S_E2) mechanism involving the formation of an intermediate which is a rate determining step.

The two steps involved are :

(*i*) Attack by electrophilic reagent Y^+ on the benzene ring to form a carbonium ion, $\overset{\oplus}{C_6A_5}{<}^{H}_{Y}$

$$C_6H_6 + Y^+ \longrightarrow \overset{\oplus}{C_6H_5}{<}^{H}_{Y} \qquad \text{(Slow)}$$

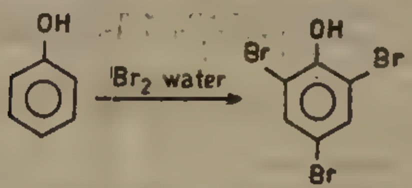
(*ii*) Removal of proton from the carbonium ion by base (: Z^- here)

$$\overset{\oplus}{C_6H_5}{<}^{H}_{Y} + :Z^- \longrightarrow C_6H_5Y + H:Z \qquad \text{(Fast)}$$

7.9. (*a*) $CH_3(CH_2)_3Br < CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 < CH_3(CH_2)_3OH < CH_3-\underset{\underset{OH}{|}}{CH}(CH_2)_2-OH$

(*b*) See section 7.7.7.

(*c*) (*i*) **Bromine water test.** Treatment of phenol with bromine water produces a pale yellow precipitate of its bromo derivative.



2 4 6-Tribromo-phenol

Ethanol does not give this test.

(*ii*) **Test with ferric chloride.** Phenols give red to purple colour when treated with neutral ferric chloride while ethanol does not produce any colour.

□ □

UNIT 8

Organic Chemistry Based on Functional Group-II

(Ethers, Aldehydes, Ketones, Carboxylic acids and their derivatives)

There is an excitement, adventure and challenge, and there can be great art, in organic synthesis.
—R.B. WOODWORD

UNIT PREVIEW

- **8.1** Introduction
- **8.2** Ethers : nomenclature, isomerism preparation, physical and chemical properties, uses
- **8.3** Aldehydes and ketones : nomenclature, isomerism, preparation, nature of carbonyl group, physical and chemical properties, commercially important carbonyl compounds, uses
- **8.4** Carboxylic acids : nomenclature, isomerism, preparation, nature of the carboxyl group, physical and chemical properties, commercially important carboxylic acids, uses
- **8.5** Derivatives of carboxylic acids
  acyl halides, acid anhydrides, acid amides and esters
  Self assessment questions
  Terminal questions
  Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Describe and give examples of the group of organic compounds called, ethers, aldehydes, ketones, carboxylic acids and their derivatives
2. Deduce the IUPAC names of the organic compounds given the structural formulae and vice-versa
3. Recognize and name the various functional groups present in the compounds included in this unit
4. Give the methods of preparation of the various compounds included in this unit
5. Correlate the variation observed in physical properties of these compounds with their structures
6. Describe the chemical reactions of these compounds

7. Comment on the strength of carboxylic acids ; and also correlate with their structures
8. Give the name reactions.
9. Describe the chemistry of some commercially important compounds included in the unit.

8.1. INTRODUCTION

The large family of organic compounds containing only the elements carbon and hydrogen is appropriately named the hydrocarbons. Hydrocarbons are of importance because they may be considered as the basis of all the organic compounds. Replacement of hydrogen atom in a hydrocarbon by an $-OH$ group gives an alcohol; a $-COOH$ group gives a carboxylic acid. It is the presence of groups such as these in the molecules that produces the dominant chemical characteristics of substances. A substance is what it is—that is, it behaves as it does chemically—because of the presence of one or more functional groups. Thus, all organic compounds can be looked on as being derived from the hydrocarbons.

In this unit, we shall study the chemistry of the following classes of carbon compounds :

Name	*General structural formula*	*Functional group*
(*a*) Ethers	$R-O-R'$	$-O-$
(*b*) Aldehydes	$\begin{matrix} R \\ H \end{matrix}\!\!>C=O$	$\begin{matrix} -C=O \\ \vert \\ H \end{matrix}$
(*c*) Ketones	$\begin{matrix} R' \\ R \end{matrix}\!\!>C=O$	$>C=O$
(*d*) Carboxylic acids and their derivatives		
(*i*) Acids	$R-\overset{\overset{O}{\Vert}}{C}-OH$	$-\overset{\overset{O}{\Vert}}{C}-OH$
(*ii*) Acyl halides	$R-\overset{\overset{O}{\Vert}}{C}-X$ (X=F, Cl, Br, I)	$-\overset{\overset{O}{\Vert}}{C}-X$
(*iii*) Acid anhydrides	$(R-\overset{\overset{O}{\Vert}}{C})_2O$	$\begin{matrix} -\overset{\overset{O}{\Vert}}{C} \\ -\underset{\underset{O}{\Vert}}{C} \end{matrix}\!\!>O$
(*iv*) Esters	$R-\overset{\overset{O}{\Vert}}{C}-OR$	$-\overset{\overset{O}{\Vert}}{C}-O-$
(*v*) Amides	$R-\overset{\overset{O}{\Vert}}{C}-NH_2$	$-\overset{\overset{O}{\Vert}}{C}-NH_2$

8.2 ETHERS

Ethers have the general formula R—O—R′ where R and R′ are alkyl or aryl groups linked by a bridging oxygen atom. Ethers may be considered as derivatives of water in which both hydrogen atoms have been replaced by alkyl or aryl groups. When the two groups attached to the oxygen atom in an ether are the same, it is said to be simple or symmetrical ether and if different, unsymmetrical or mixed ether,

$C_2H_5-O-C_2H_5$ Diethyl ether (simple)

$CH_3-O-C_2H_5$ Ethyl methyl ether (mixed)

8.2.1 Nomenclature

In the trivial or common system of nomenclature, ethers are named according to the two alkyl or aryl groups attached to the oxygen atoms :

CH_3-O-CH_3 Dimethyl ether

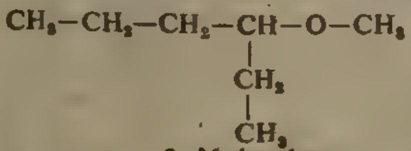
$CH_3-O-C_2H_5$ Ethyl methyl ether

$C_6H_5-O-C_6H_5$ Diphenyl ether

$C_6H_5-O-CH_3$ Methyl phenyl ether (Anisole)

According to IUPAC system the RO group (alkoxy) is regarded as a substituent of alkanes. For a ether, the larger group is chosen as the parent alkane and the smaller one as a part of the alkoxy group. For example,

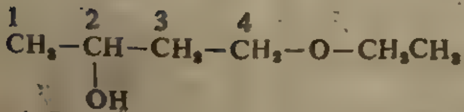
Ether	*Parent hydrocarbon*	*Name of ether*
CH_3-O-CH_3	CH_3-H	Methoxy methane
$CH_3-O-C_2H_5$	C_2H_5-H	Methoxy ethane
$C_6H_5-O-C_6H_5$	C_6H_5-H	Phenoxy benzene
$C_6H_5-O-CH_3$	C_6H_5-H	Methoxy benzene



3—Methoxyhexane

$CH_3O-CH_2-CH_2-OCH_3$

1, 2—Dimethoxyethane



4—Ethoxy—2—butanol

8.2.2. Isomerism

Ethers exhibit functional isomerism with alcohols with the same number of carbon atoms.

For example, an ether with molecular formula $C_4H_{10}O$ represents one or more isomeric alcohols.

$$\underset{\text{Diethyl ether}}{CH_3CH_2O\,CH_2CH_3} \quad \underset{n-\text{Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \quad \underset{sec-\text{Butyl alcohol}}{CH_3CH_2-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3}$$

Ethers also show metamerism due to the presence of unequal number of carbon atoms on either side of the ethereal oxygen. For example,

Simple ether	Mixed ether
$CH_3\,CH_2O\,CH_2CH_3$ (Diethyl ether)	$CH_3O\,CH_2CH_2CH_3$ Methyl-n-propyl ether
	$CH_3-O-CH(CH_3)_2$ Isopropyl methyl ether

8.2.3. Preparation of Ethers

(*i*) **Williamson synthesis** : This process involves the reaction of an alkyl or aryl halide with sodium alkoxide or phenoxide. Tke reaction involves nucleophilic replacement of the halogen atom by the alkoxide group.

$$\underset{\text{Alkyl halide}}{RX}+\underset{\text{Sodium alkoxide}}{RONa}\longrightarrow\underset{\text{Ether}}{ROR'}+NaX$$

$$RO^-+R'-X\longrightarrow \overset{\delta-}{RO}-R'-\overset{\delta-}{X}\rightarrow R-O-R'+X^-$$

For example : $\underset{\text{Ethyl chloride}}{C_2H_5-Cl}+\underset{\text{Sodium ethoxide}}{C_2H_5ONa}\longrightarrow\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5}+NaCl$

Both simple and mixed ethers may be produced by this reaction.

This method has the advantage that it proves the structure of ethers and is important for the preparation of mixed ethers. To prepare a mixed ether in which one of the alkyl groups is primary and the other is secondary or tertiary, the secondary or tertiary alkyl group is introduced using the corresponding alkoxide while the primary alkyl group is introduced using the corresponding halide. This is because secondary and tertiary halides undergo elimination in the presence of a base (*e.g.*, sodium alkoxide or sodium phenoxide) to form an alkene.

$$(CH_3)_2CHCl \xrightarrow{RO^-} CH_3-CH=CH_2$$

$$(CH_3)_3CBr \xrightarrow{RO^-} (CH_3)_2C=CH_2$$

$$C_2H_5Br + CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O^-Na^+ \rightarrow C_2H_5-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$

Ethyl bromide   Sodium-tert-butoxide   Ethyl-tert butyl ether

(*ii*) **Williamson continuous etherification process (Dehydration of alcohols).** This involves the dehydration of alcohol using concentrated H_2SO_4 (or glacial H_3PO_4). The ether and water are removed by distillation as fast as fresh alcohol is added.

The reaction involves the removal of one molecule of H_2O from two molecules of alcohol :

$$2C_2H_5OH \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4,\ 413\text{ K}} C_2H_5-O-C_2H_5 + H_2O$$

Excess of alcohol is used to avoid the formation of alkanes.

If the temperature increases to 423 K, alkenes are obtained in good amount. At 433 K, the intramolecular dehydration of alcohol mainly gives ethylene.

$$\underset{\text{Alcohol}}{C_2H_5OH} \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4,\ 433\text{ K}} \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

At 413 K, both primary and secondary alcohols give ethers. But at this temperature, tertiary alcohols mainly give alkenes.

This method is employed for the industrial production of diethyl ether. A mixture of the reactants in equimolar proportion is heated by superheated steam when ether distills over. This method produces simple ethers only.

(*iii*) **By using diazomethane.** Diazomethane reacts with hydrogen of alcohol and converts it into $-CH_3$ group giving an ether.

$$\underset{\text{Alcohol}}{ROH} + \underset{\text{Diazomethane}}{CH_2N_2} \longrightarrow \underset{\text{Ether}}{ROCH_3} + N_2$$

For example :

$$\underset{\text{Alcohol}}{C_2H_5OH} + \underset{\text{Diazomethane}}{CH_2N_2} \longrightarrow \underset{\text{Ethyl methyl ether}}{C_2H_5OCH_3} + N_2$$

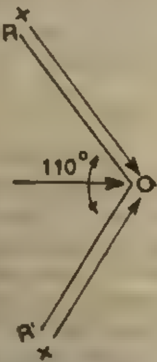
8.2.4. Physical Properties of Ethers

The lower members of the series are volatile, and sweet smelling liquids. They are highly inflammable.

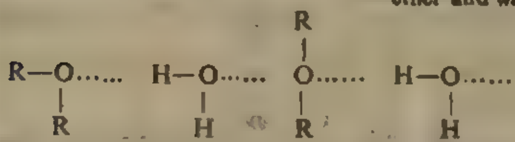
Ethers possess an angular structure with $C-\hat{O}-C$ bond angle of about 110°. Thus, they acquire slight polarity and show dipole moments of 1·2 to 1·3D. However, this weak polarity does not affect the boiling points of ethers. Their boiling points are comparable with alkenes of comparable molecular masses but are much

lower than alcohols with similar molecular masses. This is because ethers are less polar than the corresponding alcohols.

They are slightly soluble in polar solvents like water. This is because of the possibility of formation of hydrogen bonds between water and ether.



Hydrogen bonding between ether and water



Ethers are freely soluble in alcohols and other common organic solvents. They are good solvents for organic compounds. Diethyl ether (bp 300 K) is widely used to extract organic compounds from plants and other natural sources.

Ethers are freely soluble in non-polar solvents like chloroform, hydrocarbon, *etc.* In this respect they are similar to hydrocarbons.

The solubility of an ether in water is increased by the presence of small amounts of alcohol, but is decreased if the water is saturated with common salt.

8.2.5. Chemical Properties and Reactions of Ethers

Ethers are quite stable, *i.e.*, their functional group, C—O—C is quite inert as compared with C—OH unit of alcohols and phenols. These are, therefore, are not acted upon by dilute acids, metallic sodium alkalis, phosphorus pentachloride, *etc.* Oxidizing as well as reducing agents have no action on them. The chemical inertness of ethers makes them potential solvent in chemical industries and synthetic chemistry.

(*i*) **Salt formation.** Since the oxygen atom has two lone pairs of electrons, ethers behave as weak bases and form oxomium salts with strong mineral acids at low temperatures.

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O + \underset{\text{(Conc.)}}{H_2SO_4} \longrightarrow \underset{\text{Oxonium salt}}{\left[\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O^{+}-H\right]} HSO_4^{-}$$

On diluting the solution oxonium salts are decomposed back to the ether and the acid.

However, if the solution of ether and conc. H_2SO_4 is heated, the ether is decomposed to yield a molecule of the alcohol and alkyl hydrogen sulphate.

$$\underset{\text{Diethyl ether}}{C_2H_5—O \,\vdots\, C_2H_5} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Alcohol}}{C_2H_5OH} + \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4}$$

With excess of sulphuric acid, only ethyl hydrogen sulphate is obtained as alcohol also reacts with H_2SO_4.

(*ii*) **Cleavage of ethers.** Ethers undergo cleavage into two units, when treated with hot concentrated hydrogen halides (HBr can also be used). Normally hydroiodic acid is used and the products depend upon the temperature of the reaction.

In cold, an alcohol and an alkyl iodide are obtained. Mixed ethers give the alkyl iodide of the smaller alkyl radical.

$$R—O—R' + HI \xrightarrow{\text{Cold } 300 \text{ K}} \left[\begin{array}{c} R—O^{+}—R' \\ | \\ H \end{array} \right] I^{-} \longrightarrow ROH + R'I$$

For example,

$$C_2H_5—O—C_3H_7 \xrightarrow{\text{Cold } 300 \text{ K}} C_2H_5I + C_3H_7OH$$

In the presence of excess acid, the alcohol formed reacts further to give alkyl halide.

When heated, both the alkyl groups are obtained as the iodides.

$$C_2H_5—O—C_3H_7 + 2HI \longrightarrow C_2H_5I + C_3H_7I + H_2O$$

Ethers which contain one aromatic and one aliphatic groups, when heated with HI, yield alkyl halide and a phenol (aromatic C—O is not easily cleaved).

$$\underset{\text{Anisole}}{CH_3O—C_6H_5} + HI \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + CH_3I$$

Ethers can also be cleaved by heating with superheated steam in the presence of dilute sulphuric acid.

$$R—O—R' + H_2O \xrightarrow{H_2SO_4} ROH + R'OH$$

(*iii*) **Peroxide Formation.** In presence of light, ethers form peroxides when stand in contact with air, by a process of 'auto-oxidation'.

$$\underset{\text{(Ether)}}{CH_3—CH_2—O—CH_2—CH_3} \underset{\text{Light}}{\xrightarrow{O_2}} \underset{\text{(Peroxide)}}{CH_3—CH_2—O—\underset{\displaystyle O—O—H}{\underset{|}{CH}}—CH_3}$$

Peroxides are unstable and explosive molecules and their presence in old samples of ether can sometimes cause explosions during distillation of such samples.

Detection of peroxide

The presence of peroxide in an ether can be detected by treating a sample first with freshly prepared ferrous ammonium sulphate solution, and then with potassium thiocyanate. If any peroxide is present it would oxidize the ferrous to ferric, which forms blood red colour due to the formation of the ferrithiocyanate ion $Fe(SCN)^{2+}$.

Removal of peroxide

Peroxides can be removed from ethers by treating them with ferrous salt solution or distilling with conc. H_2SO_4.

It is essential to remove peroxide from ether which is to be used as an anaesthetic in surgery.

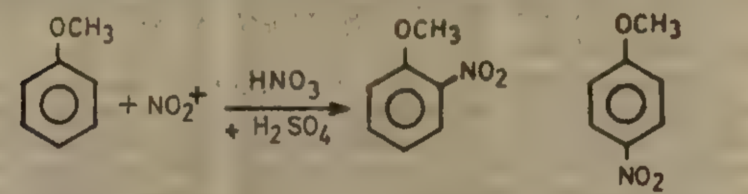
(*iv*) **Reaction due to the alkyl or aryl group.** The alkyl group behaves like a hydrocarbon.

1. **Halogenation.** Alkyl ethers, under appropriate conditions, react with chlorine or bromine forming halogenated derivatives.

$$C_2H_5{-}O{-}C_2H_5 + Cl_2 \xrightarrow{-HCl} CH_3{-}\underset{\substack{|\\ Cl}}{CH}{-}O{-}CH_2CH_3$$

Monochlorodiethyl ether

2. **Ring substitution in aromatic ethers.** Since the alkoxy (—O—R) group is ortho and para directing, aromatic ethers undergo electrophilic substitution in the benzene ring at the ortho and para-positions.



Anisole Nitronium ion o-Nitroanisole p-Nitroanisole

8.2.6. Uses of Ethers

1. Though ethers are highly inflammable, diethyl ether is still sometimes used as an anaesthetic.
2. As a solvent for carrying out Grignard* reactions.

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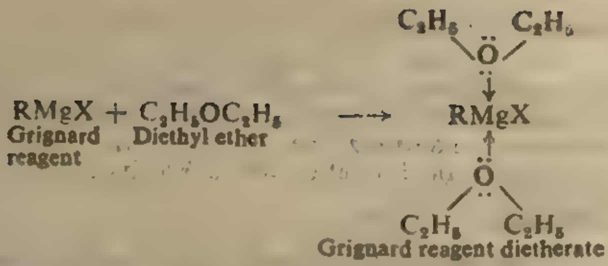
*Diethyl ether dissolves Grignard reagents because of the formation of a dietherate by donation of lone pair of electrons by the ethers to complete the octet around magnesium.



3. As an industrial solvent for resins, oils, fats and gums.
4. It has been used as a refrigerant.

8.3. ALDEHYDES AND KETONES

Aldehydes and ketones are the first oxidation products of primary and secondary alcohols respectively. They constitute two isomeric series of carbon compounds, with the general formula $R-\overset{\overset{O}{\|}}{C}-H$ for aldehydes and $R-\overset{\overset{O}{\|}}{C}-R'$ for ketones. Here R and R' could be alkyl or aryl groups and they could be same or different. The $>C=O$ group is the functional group and is called carbonyl group. The single hydrogen atom attached to this group also displays a special reactivity and is responsible for the differences between the chemical properties of aldehydes and ketones.

Formaldehyde is the smallest molecule in which the $>C=O$ group is attached to two hydrogen atoms (one hydrogen is in place of R and the other is a part of aldehydic group).

8.3.1. Nomenclature

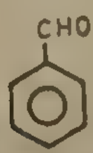
Aldehydes : The common (trivial) names of aldehydes are based on the trivial names of the carboxylic acids obtained on the oxidation of aldehydes. The '-ic acid' part of the acid is replaced by the suffix -'aldehyde'. Thus, the compound which forms acetic acid on oxidation is called acetaldehyde. The IUPAC system demands the

Formula of aldehyde	*Acid to which oxidized*		*Name of aldehyde*
	Formula	*Name*	
$HCHO$	$HCOOH$	Formic acid	Formaldehyde
CH_3-CHO	CH_3-COOH	Acetic acid	Acetaldehyde
CH_3-CH_2-CHO	CH_3-CH_2-COOH	Propionic acid	Propionaldehyde
$CH_3(CH_2)_2CHO$	$CH_3(CH_2)_2-COOH$	n-Butyric acid	n-Butyraldehyde

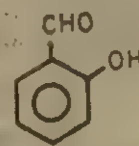
ending -al with the suffix. The longest chain containing the $-CHO$ group is selected as the parent hydrocarbon and the name is obtained by replacing the last '*e*' of the alkane by 'al'. The carbon of the $-CHO$ group is given the number 1. For example,

Formula	*Parent hydrocarbon*	*IUPAC name*
$HCHO$	$H-CH_3$	Methanal
CH_3-CHO	CH_3-CH_3	Ethanal
CH_3-CH_2-CHO	$CH_3-CH_2-CH_3$	Propanal
$CH_3-CH_2-CH_2-CHO$	$CH_3-CH_2-CH_2-CH_3$	n-Butanal
$CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-CHO$	$CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	2-Methylbutanal

The names of the aromatic aldehydes may be derived form the simplest aromatic aldehyde benzaldehyde :



Benzaldehyde



o-Hydroxybenzaldehyde
(Salicylaldehyde).

Ketones : The common (trivial) names of ketones are derived from the alkyl groups attached to carbonyl carbon followed by the word ketone. Symmetrical ketones are named as dialkyl ketones. Unsymmetrical ketones are named by naming the alkyl groups as separate words in alphabetic order. The simplest ketone, $(CH_3)_2CO$ is called acetone. The names of some other ketones are as follows :

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$
Ethyl methyl ketone

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$
Diethyl ketone

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$$
Methyl n-propyl ketone

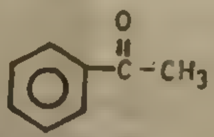
$$C_2H_5-\overset{\overset{O}{\|}}{C}-CH(CH_3)_2$$
Ethyl isoproyl ketone

The IUPAC system demands the ending -one with the suffix. The longest chain containing the ketonic function is selected as the parent hydrocarbon and the name is obtained by replacing the last 'e' of the alkane by -one. The parent chain is numbered from that end which will give the lowest number to the carbon of carbonyl group.

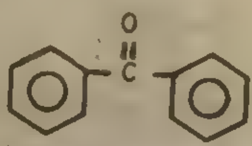
For example :

Formula	*Parent hydrocarbon*	*IUPAC name*
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	$CH_3-CH_2-CH_3$	Propanone
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$	$CH_3-CH_2-CH_2-CH_3$	2-Butanone
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$	$CH_3-CH_2-CH_2-CH_2-CH_3$	2-Pentanone
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{\underset{\|}{CH_2}}}{\underset{\|}{CH}}-CH_3$	$CH_3-CH_2-CH_2-\underset{\underset{CH_3}{\underset{\|}{C_2H_4}}}{\underset{\|}{CH}}-CH_3$	4-Methyl-3-Hexanone

Two simple aromatic ketones are :



Methyl phenyl ketone, or Acetophenone



Diphenyl ketone, or Benzophenone

Sometimes, while naming substituted carbonyl compounds, the position of side chains or substituents on the parent chain are denoted by Greek letters, α, β, γ, δ *etc*. The carbon adjacent to the $>C=O$ is called α, the one next to it β and so on. Thus

$$\overset{\gamma}{C}H_3-\overset{\beta}{C}H_2-\underset{\underset{Cl}{|}}{\overset{\alpha}{C}H}-CHO$$

α-Chlorobutanal

$$\overset{\beta}{C}H_3-\underset{\underset{Cl}{|}}{\overset{\alpha}{C}H}=\overset{\overset{O}{\|}}{C}-CH_3$$

α-Chlorobutanone

$$HO\,\overset{\alpha'}{C}H_2-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{C}H_2OH$$

α, α'-Dihydroxy-propanone

8.3.2. Isomerism

Aldehydes and ketones show chain isomerism, *e.g.*, n-butyraldehyde, $CH_3-CH_2-CH_2-CHO$ and isobutyraldehyde $(CH_3)_2-CH-CHO$ are chain isomers ; methyl n-propyl ketone,

$CH_3-CO-CH_2-CH_2CH_3$ and isopropyl methyl ketone, $CH_3-CO-CH-(CH_3)_2$ are chain isomers.

Ketones alone also exhibit positional isomerism due to the difference in placement of $-\overset{O}{\overset{\|}{C}}-$ in the carbon chain. For example,

$$\underset{\text{2-Pentanone}}{\overset{1}{C}H_3-\underset{\underset{O}{\|}}{\overset{2}{C}}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3} \qquad \underset{\text{3-Pentanone}}{\overset{1}{C}H_3-\overset{2}{C}H_2-\underset{\underset{O}{\|}}{\overset{3}{C}}-\overset{4}{C}H_2-\overset{5}{C}H_3}$$

Ketones also show functional isomerism with aldehydes and unsaturated alcohols. For example, the ketone with molecular formula C_3H_6O represents the following compounds :

$$\underset{\text{Acetone}}{CH_3-CO-CH_3} \qquad \underset{\text{Propanal}}{CH_3-CH_2-CHO} \qquad \underset{\text{Allyl alcohol}}{CH_2=CH-CH_2-OH}$$

8.3.3. Preparation of Aldehydes and Ketones

Aldehydes and ketones are prepared by the following methods :

(*i*) **Oxidation of alcohols** : Alcohols can be oxidized in two ways :

(*a*) **By direction oxidation**

Aldehydes can be prepared by the oxidation of primary alcohols, using an oxidizing agent such as acidified potassium dichromate or potassium p rmanganate. Aldehydes are oxidized to carboxylic acids even more earlier than alcohols from which they are derived. To prevent this oxidation, aldehyde formed must be removed from the oxidizing medium. Since they have lower boiling points than the parent alcohols, this is accomplished by distillation.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}+[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3CHO}+H_2O$$

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}+[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Benzaldehyde}}{C_6H_5CHO}+H_2O$$

Ketones are obtained by the oxidation of secondary alcohols. Potassium dichromate in dilute H_2SO_4 is the usual oxidizing agent. Unlike aldehydes, ketones are not easily oxidized ; therefore no special technique is necessary to prevent further oxidation to an acid.

$$\underset{\text{Isopropyl alcohol}}{\begin{matrix}CH_3\diagdown\\ \quad CHOH\\ CH_3\diagup\end{matrix}}+[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetone}}{\begin{matrix}CH_3\diagdown\\ \quad C=O\\ CH_3\diagup\end{matrix}}+H_2O$$

Oxidation of secondary alcohol can also be done by **Oppenauer oxidation**, which involves the refluxing of alcohol with acetone in the presence of aluminium tert-butoxide as catalyst.

$$\underset{\text{Secondary alcohol}}{\begin{matrix}R\\ \rangle CHOH\\ R'\end{matrix}} + \underset{\text{Acetone}}{\begin{matrix}CH_3\\ \rangle C{=}O\\ CH_3\end{matrix}} \xrightarrow{\text{Catalyst}} \underset{\text{Ketone}}{\begin{matrix}R\\ \rangle C{=}O\\ R'\end{matrix}} + \underset{\text{Isopropyl alcohol}}{\begin{matrix}CH_3\\ \rangle CHOH\\ CH_3\end{matrix}}$$

In this reaction, acetone gets reduced to isopropyl alcohol. This method is not suitable for the preparation of aldehydes as they undergo condensation.

(*b*) **By catalytic dehydrogenation**

When vapours of primary and secondary alcohols are passed over heated copper gauze (or silver metal), they are dehydrogenated to corresponding aldehydes and ketones respectively.

$$\underset{\text{Primary alcohol}}{R\,CH_2\,OH} \xrightarrow[573K]{Cu} \underset{\text{Aldehyde}}{R\,CHO} + H_2$$

$$\underset{\text{Secondary alcohol}}{\begin{matrix}R\\ \rangle CHOH\\ R\end{matrix}} \xrightarrow[573K]{Cu} \underset{\text{Ketone}}{\begin{matrix}R\\ \rangle{=}O\\ R\end{matrix}} + H_2O$$

For example :

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[573K]{Cu} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$$

$$\underset{\text{sec-Butyl alcohol}}{\begin{matrix}CH_3\\ \rangle CHOH\\ CH_3CH_2\end{matrix}} \xrightarrow[573K]{Cu} \underset{\text{Methyl ethyl ketone}}{\begin{matrix}CH_3\\ \rangle C{=}O\\ CH_3CH_2\end{matrix}}$$

This method has the advantage that no further oxidation occurs.

(*ii*) **By hydrolysis of gemdihalides.** The dihalides containing halogens on the same carbon atoms at the end of the chain ($-CHCl_2$) on hydrolysis with aqueous potassium hydroxide yield **aldehydes.**

$$\underset{\substack{\text{1, 1-Dichloroethane}\\ \text{(Gemdichloroethane)}}}{H_3C-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}H} \xrightarrow[KOH]{HOH} \underset{\text{(Unstable glycol)}}{\left[H_3C-\overset{\displaystyle OH}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-H \right]} \xrightarrow{-H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

If the two halogens are attached to a carbon present in the middle of the chain, a **ketone** is obtained.

$$\underset{\text{2, 2-Dichloropropane}}{CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3} \xrightarrow[KOH]{HOH} \underset{\text{(Unstable glycol)}}{\left[CH_3-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3\right]} \xrightarrow{-H_2O} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

(*iii*) **By decarboxylation of acids and their salts.** Decarxylation of acids and their salts is done in two ways :

(*a*) **By reduction of acids and their salts**

Aldehydes can be prepared by catalytic reduction of an acid chloride with hydrogen, using a palladium catalyst deposited on barium sulphate.

This reaction is known as Rosenmund reduction.

$$\underset{\text{Acid chloride}}{RCOCl}+H_2 \xrightarrow{\text{Pd on }BaSO_4} \underset{\text{Aldehyde}}{R.CHO} \quad +HCl$$

For example :

$$\underset{\text{Acetylchloride}}{CH_3COCl}+H_2 \xrightarrow{\text{Pd on }BaSO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \quad +HCl$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow{\text{Pd on }BaSO_4} \underset{\text{Benzaldehyde}}{C_6H_5CHO}+HCl$$

The catalyst is of significance since it has to speed up the replacement of the chlorine in the acid chloride by hydrogen and yet must not favour the reduction of aldehyde. Rosenmund gave the palladium catalyst whose efficiency was impaired (*i.e.*, a poisoned catalyst) by the presence of barium sulphate.

Ketones can be prepared from acid chlorides using organocadmium compounds.

$$2\underset{\substack{\text{Acid}\\\text{chloride}}}{RCOCl}+\underset{\substack{\text{Dialkyl}\\\text{cadmium}}}{Cd\,R_2'} \longrightarrow 2\underset{\text{Ketone}}{RCOR'}+CdCl_2$$

Organocadmium compounds are obtained on treating Grignard reagent with dry cadmium chloride.

$$\underset{\text{Grignard reagent}}{2R'MgX}+CdCl_2 \longrightarrow \underset{\text{Dialkyl cadmium}}{R'_2Cd} \quad +2Mg\,XCl$$

For example :

$$2\underset{\substack{\text{Propanoyl}\\\text{chloride}}}{C_2H_5COCl}+\underset{\substack{\text{Dimethyl}\\\text{cadmium}}}{Cd\,(CH_3)_2} \longrightarrow \underset{\text{Ethyl methyl ketone}}{2C_2H_5-COCH_3}+CdCl_2$$

(*b*) **By dry distillation of calcium salts of fatty acids**

Calcium salt of a carboxylic acid on distillation with calcium formate gives an aldehyde.

$$\underset{\text{Acid acetate}}{(RCO_2)_2Ca} + \underset{\text{Calcium formate}}{(HCO_2)_2Ca} \longrightarrow 2CaCO_3 + \underset{\text{Aldehyde}}{2RCHO}$$

For example :

$$\underset{\text{Calcium acetate}}{(CH_3CO_2)_2Ca} + (HCO_2)_2Ca \longrightarrow 2CaCO_3 + \underset{\text{Acetaldehyde}}{2CH_3CHO}$$

The yield in most cases is low, and formaldehyde and a ketone are formed as side products. Calcium salt of a carboxylic acid (other than formic acid) on dry distillation gives ketone.

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \longrightarrow \underset{\text{Acetone}}{\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C=O} + CaCO_3$$

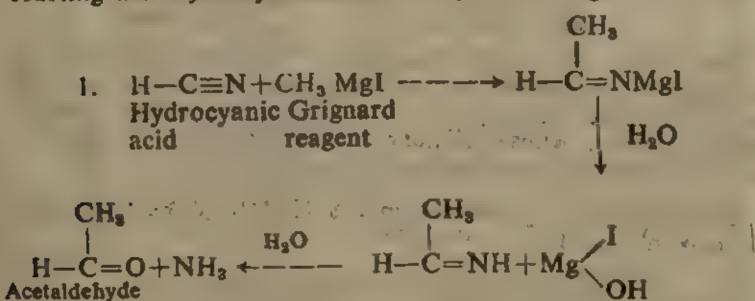
The yield of ketone is often low. Mixed ketones are obtained by heating a mixture of calcium salts of two carboxylic acids (not formic acid).

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium propionate}}{(C_2H_5COO)_2Ca} \longrightarrow \underset{\text{Ethyl methyl ketone}}{CH_3COC_2H_5}$$

The product is accompanied by the corresponding ketones of the two salts.

(*vi*) **By using Gringard reagents.** Grignard reagent on reacting with hydrocyanic acid or ethyl formate gives an **aldehyde**.

1.



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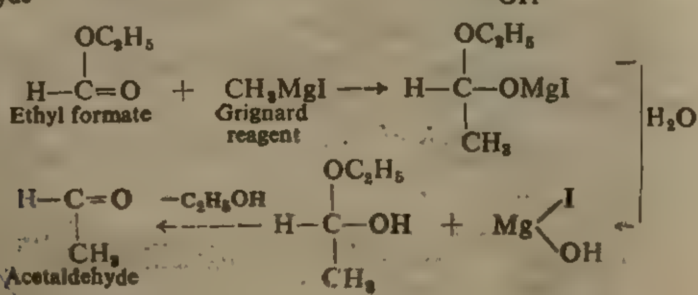


A Grignard reagent on reacting with alkyl cyanide (say methyl cyanide) or acid chloride gives **ketone.**

1. $$\underset{\text{Methyl cyanide}}{CH_3-C\equiv N}+\underset{\text{Grignard reagent}}{CH_3MgI} \longrightarrow CH_3-\overset{\overset{\Large CH_3}{|}}{C}=NMgI$$

$$CH_3-\overset{\overset{\Large CH_3}{|}}{C}=NMgI \xrightarrow{H_2O} CH_3-\overset{\overset{\Large CH_3}{|}}{C}=NH+Mg\begin{matrix}\diagup I\\ \diagdown OH\end{matrix}$$

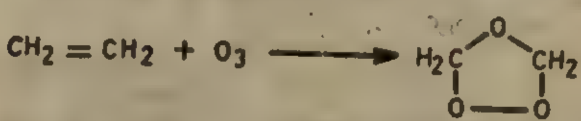
$$CH_3-\overset{\overset{\Large CH_3}{|}}{C}=NH \xrightarrow{H_2O} \underset{\text{Acetone}}{CH_3-\overset{\overset{\Large CH_3}{|}}{C}=O}+NH_3$$

2. $$\underset{\text{Propanoyl chloride}}{C_2H_5-\underset{\underset{\Large Cl}{|}}{C}=O}+\underset{\text{Grignard reagent}}{CH_3MgI} \longrightarrow C_2H_5-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large Cl}{|}}{C}}-O\,MgI$$

$$\xrightarrow{H_2O} HOMg\,I + HCl + \underset{\text{Ethyl methyl ketone}}{CH_3-CO-C_2H_5}$$

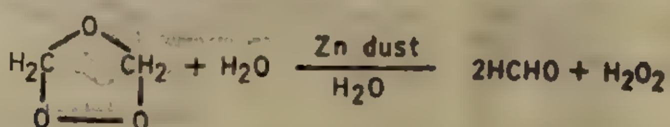
(*v*) **By ozonolysis of alkenes.** Alkenes on reacting with ozone form ozonides which on reduction with zinc and water yields aldehydes are ketones or a mixture of both.

When ozone is passed through a solution of alkenes in an inert solvent the latter gets oxidized forming explosive ozonide. This reaction is known as "**ozonolysis**". For example,



Ethylene ozonide

The ozonide, on treatment with water, in presence of zinc dust undergoes decomposition yielding aldehydes or ketones depending upon the nature of ozonides.



Formaldehyde

The products, thus, produced can often be used to determine the structure of unknown alkene. The following reactions illustrate the point.

$$CH_3-CH=C\langle^{CH_3}_{CH_3} \xrightarrow[(ii)\ Zn,\ H_3O^+]{(i)\ O_3} CH_3-CH=O+O=C\langle^{CH_3}_{CH_3}$$

$$CH_3-CH_2-CH=C\langle^{CH_3}_{CH_3} \xrightarrow[(ii)\ Zn,\ H_3O^+]{(i)\ O_3} CH_3CH_2=O+O=C\langle^{CH_3}_{CH_3}$$

$$CH_3-CH_2-CH=CH-CH_3 \xrightarrow[(ii)\ Zn,\ H_3O^+]{(i)\ O_3}$$

$$CH_3-CH_2-CH=O+O=C\langle^{H}_{CH_3}$$

$$CH_3-CH_2-CH_2-CH=CH_2 \xrightarrow[(ii)\ Zn,\ H_3O^+]{(i)\ O_3}$$

$$CH_3-CH_2-CH_2\ CH=O+O=CH_2$$

8.3.4. Preparation of Aromatic Aldehydes and Ketones

Preparation of aromatic aldehydes

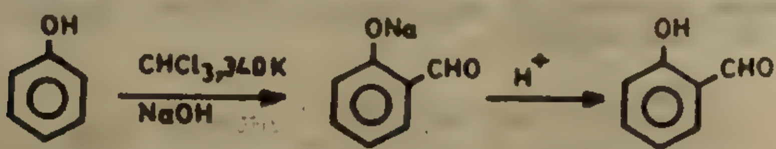
Some methods applicable for the preparation of aromatic aldehydes are as under :

(*i*) **Oxidation of side-chain alkyl groups.** Toluene when oxidized with chromium trioxide in acetic anhydride forms benzylidene acetate, *i.e.*, a derivative of benzaldehyde. This prevents further oxidation of benzaldehyde to benzoic acid. The benzylidene acetate may be hydrolyzed with dil. HCl to benzaldehyde.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[(CH_3CO)_2O]{CrO_3} \underset{\text{Benzylidene acetate}}{C_6H_5CH\ (OCOCH_3)_2} \xrightarrow{\text{Dil. HCl}}$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+2CH_3COOH$$

(*ii*) **Reimer-Tiemann reaction.** Salicylaldehyde can be prepared by treating phenol with chloroform and sodium hydroxide at 340 K. This reaction has already been discussed in Unit 7, p. 332.



Salicylaldehyde

Preparation of aromatic ketones

Aromatic ketones can be prepared by a Friedel Craft's acylation reaction. An aromatic hydrocarbon is treated with an acid chloride in the presence of anhydrous aluminium chloride :

$$C_6H_5-\boxed{-H+Cl-}-COCH_3 \xrightarrow[AlCl_3]{\text{Anhydrous}} C_6H_5COCH_3+HCl$$

Acetyl chloride Acetophenone

$$C_6H_6+C_6H_5COCl \xrightarrow[AlCl_3]{\text{Anhydrous}} C_6H_5COC_6H_5$$

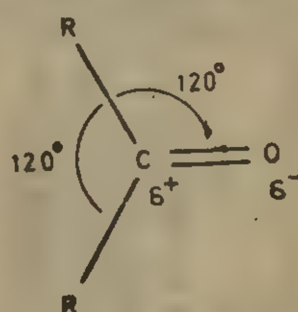
Benzoyl chloride Benzophenone

Important methods of preparing aldehydes and ketones are summarized in Fig. 8·1.

8.3.5. Nature of the Carbonyl Group

The carbonyl group has a geometry similar to that of the carbon-carbon double bond in alkenes.

The carbonyl group has a double bond between carbon and oxygen and because of a difference in electronegativity between these two, the π-electrons are not equally shared. Oxygen being more electronegative, the electron cloud is polarized towards the oxygen, which pulls the mobile π-electrons to itself. This polarization of electrons results in a high dipole moment (2 3 to 2.8 D) for carbonyl compounds. The $>C=O$ double bond thus differs from $-C=C-$ bond of alkenes which is non-polar in nature.



The carbon atom of $>C=O$ is sp^2 hybridized and is joined to three bonds which lie in a plane making an angle of 120° with one another.

8.3.6. Physical Properties of Carbonyl Compounds

Formaldehyde is a gas while other common aldehydes and ketones are liquids at room temperature. Aldehydes and ketones are polar compounds because of the presence of carbonyl group. Their boiling points increase with the increase of molecular mass.

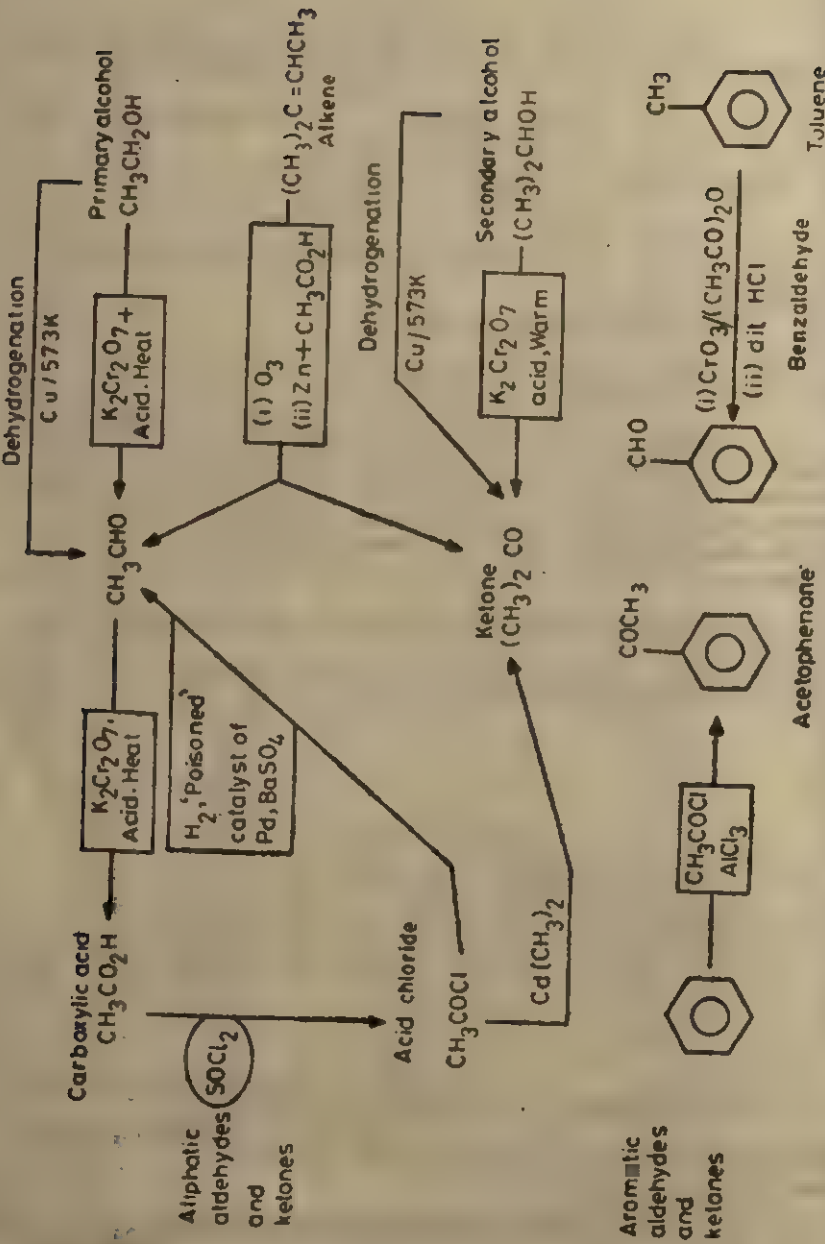


Fig. 8·1. Important methods of preparing aldehydes and ketones.

The boiling points are higher than the alkanes and ethers of comparable molecular masses (Table 8·1). This is the result of intermolecular attractions between the molecules. The extent of intermolecular attraction is smaller than the hydrogen bonding in corresponding alcohols (Fig. 8·2). Therefore, aldehydes and ketones are lower boiling liquids than alcohols and carboxylic acids of comparable molecular masses.

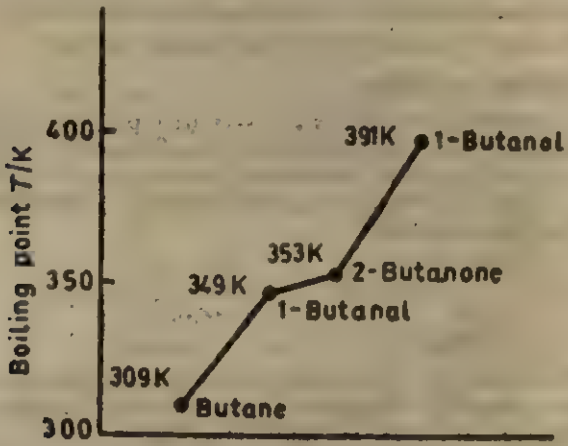


Fig. 8·2. Boiling points of aldehydes and ketones are lower than corresponding alcohols.

TABLE 8·1

Name	*Formula*	*Boiling point* (K)	*Molecular mass*
n-Butane	$CH_3-CH_2-CH_2-CH_3$	273	58
Methyl ethyl ether	$CH_3-O-CH_2-CH_3$	281	60
Propionaldehyde	C_2H_5-CHO	322	58
Acetone	$CH_3-CO-CH_3$	329	58
n-Propyl alcohol	$C_2H_5-CH_2OH$	371	60
Propionic acid	CH_3-CH_2COOH	391	60

The lower aldehydes and ketones are soluble in water, but as the size of the alkyl groups increases, solubility decreases. Solubility of lower aldehydes and ketones is attributed to intermolecular hydrogen bonding between carbonyl group and water molecules. Aldehydes and ketones are quite soluble in organic solvents.

Aldehydes with smaller alkyl groups have choking smell but ketones have pleasant smell. Some higher aldehydes and ketones have pleasant smell.

8.3.7. Chemical Reactions

There are certain chemical reactions which are common to both aldehydes and ketones, but others are shown either by aldehydes or ketones. The reactions of aldehydes and ketones are dominated by the $>C=O$ group.

(a) Reactions common to aldehydes and ketones

These are the reactions of the carbonyl group.

1. Addition reactions

The double bond of the $>C=O$ group is a point of unsaturation permitting the addition of a variety of reagents. Attack occurs via the partially positive electron deficient carbonyl carbon (becaeue of pull of electrons by oxygen), which attracts nucleophilic reagnst (supply an electron pair).

$$\underset{\text{Aldehyde}}{\begin{matrix} R \\ H \end{matrix}\!\!>\!\overset{+\delta}{C}=\overset{-\delta}{O}} \qquad \underset{\text{Ketone}}{\begin{matrix} R \\ R \end{matrix}\!\!>\!\overset{+\delta}{C}=\overset{-\delta}{O}}$$

For some of the lower carbonyl compounds the reactivity towards nucleophiles decrease in the order (alkyl groups are electron repelling, *i.e.* they show +I inductive effect).

$$\begin{matrix} H \\ H \end{matrix}\!\!>\!C=O \;>\; \begin{matrix} CH_3 \\ H \end{matrix}\!\!>\!C=O \;>\; \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=O \;>\; \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!C=O$$

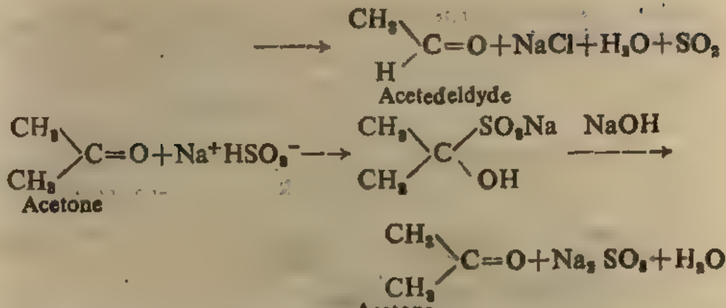
(*i*) **Addition of sodium hydrogen sulphite :** Aldehydes and ketones react with sodium hydrogen sulphite (sodium bisulphite) forming addition compounds. The addition product on treatment with acids or alkalis regenerate the original carbonyl compound. This provides a means of separation and purification of aldehydes and ketones.

$$\underset{\substack{\text{Carbonyl}\\\text{compound}}}{>C=O} + Na^+HSO_3^- \longrightarrow \underset{\substack{\text{Bisulphite}\\\text{compound (crystalline)}}}{>C\!\!<\!\begin{matrix} SO_3H \\ O^-\,Na^+ \end{matrix}}$$

$$\xrightarrow{\text{Proton transfer}} \begin{matrix} OH \\ Na^+O_3^-S \end{matrix}\!\!>\!C{-}O \xrightarrow[OH^-]{H^+} \text{Carbonyl compound}$$

For example :

$$\underset{\text{Acetaldehyde}}{\begin{matrix} CH_3 \\ H \end{matrix}\!\!>\!C=O} + Na^+HSO_3^- \longrightarrow \begin{matrix} CH_3 \\ H \end{matrix}\!\!>\!C\!\!<\!\begin{matrix} SO_3Na \\ OH \end{matrix} \xrightarrow{HCl}$$

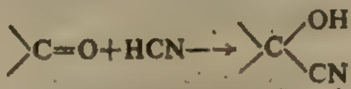


Acetedeldyde

Acetone

Acetone

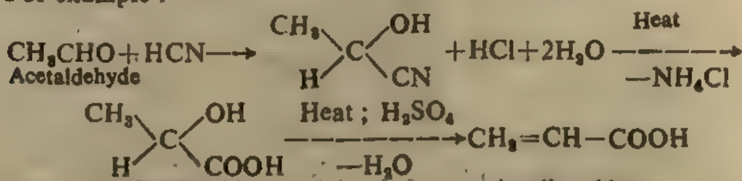
(*ii*) **Addition of hydrogen cyanide** : Hydrogen cyanide forms cyanohydrins under basic conditions with both aldehydes and ketones.



Cyanohydrin

By means of this reaction an extra carbon is introduced into the molecule. The cyanohydrins are useful intermediates in the synthesis of α-hydroxy acids, unsaturated acids and amino acids.

For example :



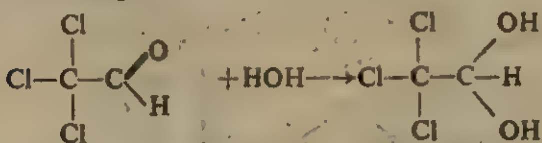
Acetaldehyde

Lactic acid

Acrylic acid

(*iii*) **Addition of water** : Hydration of an aldehyde or ketone produces a highly unstable dihydroxy compouud. But halogenated aldehydes and ketones give stable products.

For example :



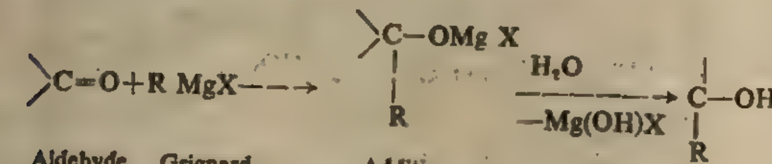
Trichloroacetaldehyde or Chloral

Chloral hydrate

The presence of the highly electronegative chlorine atoms stabilises the molecule.

(*iv*) **Addition of Grignard reagent** : Grignard reagent reacts with aldehydes and ketones to form an addition product which on hydrolysis yields a primary, a secondary or a tertiary

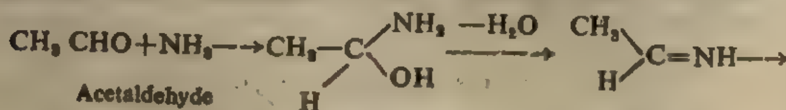
alcohol (discussed earlier under general methods of preparation of alcohols, Unit 7)



Aldehyde or ketone — Grignard reagent — Addition product — Alcohol

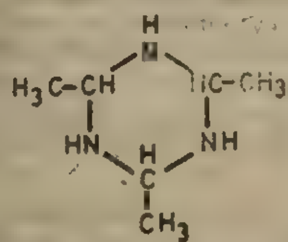
(v) **Addition of ammonia**

Aldehydes other than formaldehyde give an addition product called an aldehyde ammonia.



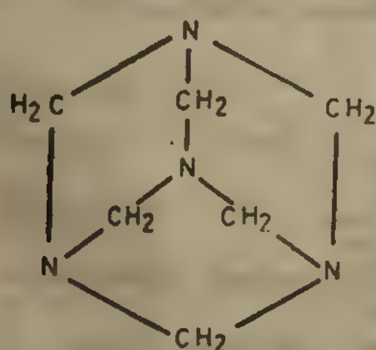
Acetaldehyde — Acetaldehyde ammonia (Unstable) — Aldimine (very reactive)

Polymerizes



Formaldehyde behaves differently and forms hexamethylene tetramine, $(CH_2)_6N_4$:

$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$



Hexamethylene tetramine

Ketones also give ketone ammonia but these can't be isolated. Acetone reacts slowly with ammonia to form first acetone ammonia at low temperature. But at higher temperature, diacetoneamine is formed.

$$\underset{\text{Diacetone ammonia}}{\overset{CH_3}{\underset{CH_3}{>}}C(NH_2)-CH_2\,COCH_3} \xleftarrow[NH_3]{\text{High temp.}} CH_3-CO-CH_3$$

$$\xrightarrow[NH_3]{\text{Low temp.}} \underset{\text{Acetone ammonia}}{(CH_3)_2C(OH)(NH_2)}$$

(*vi*) **Addition of ammonia derivatives followed by loss of water** : The $>C{=}O$ of aldehydes and ketones undergo reactions with a number of organic compounds containing $-NH_2$ group with the elimination of water.

(*i*) **Reduction with hydroxylamine** : This reacts to yield condensation products called oximes :

$$\underset{\text{Carbonyl compound}}{>C{=}O} + H_2N-OH \longrightarrow \underset{\text{Oxime}}{>C{=}N-OH} + H_2O$$

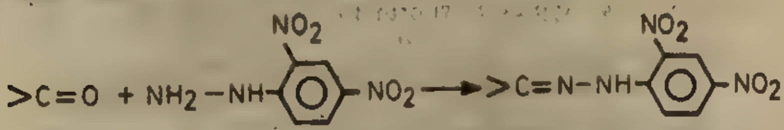
$$\underset{\text{Acetaldehyde}}{CH_3CH{=}O} + H_2-N-OH \longrightarrow \underset{\text{Acetaldoxime}}{CH_3-CH{=}N-OH} + H_2O$$

$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + H_2-N-OH \longrightarrow \underset{\text{Dimethylketoxime}}{(CH_3)_2\,C{=}N-OH} + H_2O$$

(*ii*) **Reaction with hydrazine, phenylhydrazine and 2, 4-dinitrophenyl hydrazine** : These react to yield the corresponding condensation hydrazones.

$$\underset{\text{Aldehyde or ketone}}{>C{=}O} + \underset{\text{Hydrazine}}{NH_2-NH_2} \longrightarrow \underset{\text{Hydrazone}}{>C{=}N-NH_2} + H_2O$$

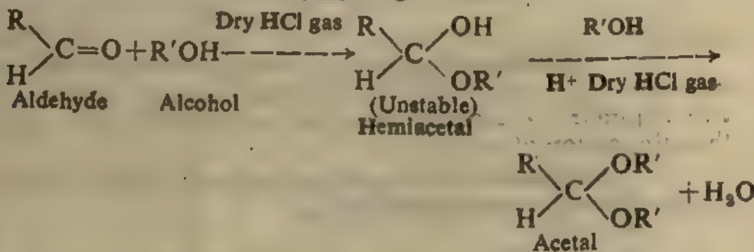
$$\underset{\text{Aldehyde or ketone}}{>C{=}O} + \underset{\text{Phenylhydrazine}}{NH_2-NH-C_6H_5} \longrightarrow \underset{\text{Phenylhydrazone}}{>C{=}N-NH-C_6H_5} + H_2O$$



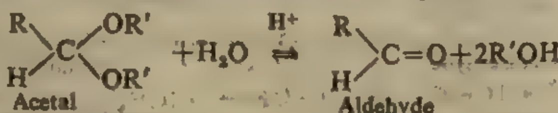
Aldehyde or ketone | 2,4-Dinitrophenyl-hydrazine | 2,4-Dinitrophenyl-hydrazone

The reagents if used as free amines are easily oxidizable by air and, therefore, are usually employed as their salts, *e g.*, hydroxyl amine hydrochloride, $NH_2OH.HCl$; phenylhydrazine hydrochloride, $C_6H_5-NH-NH_2.HCl$, *etc.* The products of reaction are mostly crystalline solids with sharp melting points. For this reason, they are frequently used for the characterization and identification of carbonyl compounds.

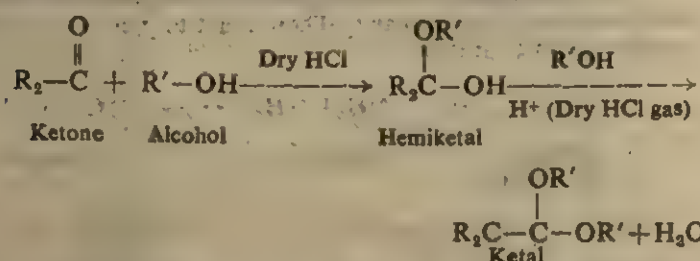
(*vii*) **Addition of alcohol followed by loss of water** : Aldehydes react with alcohols first to form a hemiacetal and then an acetal in the presence of dry hydrogen chloride.



Actually this is an equilibrium reaction, *i.e.*, acetals can be broken down back to the aldehydes with the help of acids.



Ketones would react to form hemiketals and ketals.



The above equilibria lie far to the left and hence ketals are not formed. Water is removed to favour the forward reaction. This is done by adding ethyl orthoformate, $HC(OC_2H_5)_3$.

$$\underset{\text{Ethyl orthoformate}}{HC(OC_2H_5)_3} + H_2O \overset{H^+}{\rightleftharpoons} 2C_2H_5OH + \underset{\text{Ethyl formate}}{HCOOC_2H_5}$$

2. Reduction reactions

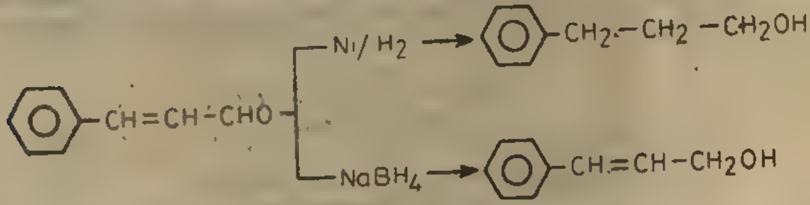
(*i*) **Reduction to alcohols** : Aldehydes are reduced to primary alcohols while ketones are reduced to secondary alcohols.

Reduction may be carried out by chemical means ($LiAlH_4$ or $NaBH_4$) or through catalytic (Pt, Pd, Ni, *etc.*) hydrogenation.

$$\underset{\text{Aldehyde}}{R\,CHO} \xrightarrow[\text{LiAlH}_4/\text{Ether}]{\text{Pt/H}_2\text{, or}} \underset{\text{Primary alcohol}}{R-\overset{\displaystyle OH}{\overset{|}{C}H}-H}$$

$$\underset{\text{Ketone}}{R-\overset{\displaystyle O}{\overset{\|}{C}}-R'} \xrightarrow[\text{NaBH}_4/\text{Ether}]{\text{Pt/H}_2\text{, or}} \underset{\text{Secondary alcohol}}{R-\overset{\displaystyle OH}{\overset{|}{C}H}-R'}$$

Catalytic hydrogenation also saturates any unsaturation present in the molecule whereas sodium borohydride reduces only the carbonyl group :



(*ii*) **Reduction to hydrocarbons** : This may be carried out in the two ways :

1. **Clemmensen reduction** : The $>C=O$ group of aldehyde or ketone is reduced to methylene group using zinc amalgam and concentrated hydrochloric acid.

$$\underset{\text{Aldehyde}}{RCHO}+4[H] \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} \underset{\text{Alkane}}{RCH_2}+H_2O$$

$$\underset{\text{Ketone}}{\begin{matrix}R\\R\end{matrix}\!\!>C=O}+4[H] \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} \underset{\text{Alkane}}{\begin{matrix}R\\R\end{matrix}\!\!>CH_2}+H_2O$$

For example :

$$\underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O}+4[H] \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} \underset{\text{Propane}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH_2}$$

2. **Wolff-Kishner reduction** : By heating the hydrazone of the carbonyl compound with sodium ethoxide at 450 K :

$$\begin{matrix}R\\H\end{matrix}\!\!>C=O \xrightarrow[-H_2O]{NH_2-NH_2} \underset{\text{Hydrazone}}{\begin{matrix}R\\H\end{matrix}\!\!>C=N-NH_2} \xrightarrow[450\text{ K}]{C_2H_5ONa} \underset{\text{Alkane}}{\begin{matrix}R\\R\end{matrix}\!\!>CH_2}+N_2$$

For example :

$$\underset{\text{Acetaldehyde}}{\overset{CH_3}{\underset{H}{>}}C=O} \xrightarrow[-H_2O]{H_2N-NH_2} \overset{CH_3}{\underset{H}{>}}C=N-NH_2 \xrightarrow[450\text{ K}]{C_2H_5ONa} \underset{\text{Ethane}}{CH_3-CH_3}+N_2$$

3. **Oxidation reactions**

(*i*) **Oxidation to carboxylic acids :** Differences in behaviour between aldehydes and ketones towards oxidizing agents constitute the main difference between aldehydes and ketones. This is because aldehydes are easily oxidizable by mild oxidizing agents like Tollen's reagent, Fehling's and Benedict's solutions and Schiff's reagent to carboxylic acids containing the same number of carbon atoms whereas ketones can be oxidized only under drastic conditions when they yield lower acids. Oxidation of ketone requires the cleavage of C—C bond.

$$RCHO \xrightarrow[\text{Mild conditions}]{[O]} RCOOH$$

$$RCH_2-CO-R \xrightarrow[\text{Drastic conditions}]{[O]} 2RCOOH$$

The presence of aldehydes can be tested by **Tollen's reagent** (ammoniacal silver nitrate solution). The complex silver ammonia ion, $[Ag(NH_3)_2]^+$ is reduced to metallic silver on warming with aldehyde. The silver mirror deposits on the walls of the container.

$$RCHO+2[Ag(NH_3)_2]OH \longrightarrow RCOOH+\underset{\substack{\text{(Silver}\\\text{mirror)}}}{2Ag}+H_2O+4NH_3$$

The presence of aldehydes can also be tested by using **Fehling's** or **Benedict's** solutions. Fehling's solution is an alkaline solution of copper sulphate containing sodium potassium tertrate (Rochelle salt) as the complexing agent. Benedict's solution is an alkaline solution of copper sulphate containing sodium citrate as complexing agent.

Aliphatic aldehydes on warming with Fehling's or Benedict ' s solution give a brick red precipitate of cuprous oxide on reduction of the alkaline Cu(II).

$$CH_3CHO+Cu(OH)_2 \longrightarrow \underset{\text{(Red precipitate)}}{Cu_2O}+2H_2O+CH_3COOH$$

The blue colour of the Fehling's solution changes to green, yellowish and finally brick red to the formation of red ppt. of Cu_2O.

Aldehydes also react with **Schiff's reagent** producing a characteristic colour. This reagent is a solution of a magenta dye which has been decolourized by passing sulphur dioxide through the

solution. Aldehydes on reacting with reagent rapidly restore colour. The reaction is a complex one and is not related to the reducing properties of aldehydes involved.

Ketones are not oxidized by the above reagents. Ketones are oxidized by alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$ to carboxylic acids.

$$\underset{\text{2-Butanone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3} \xrightarrow{KMnO_4} \underset{\text{Acetic acid}}{2CH_3COOH}$$

α-Carbon atom with fewer hydrogen atoms is attacked in preference to the other (Popoff's rule). If the α-carbon atom adjacent to >C=O have the same number of hydrogen atoms, the >C=O group remains chiefly with the smaller alkyl group. For example,

$$\underset{\text{Hexan-3-one}}{CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2\ CH_3} \longrightarrow \underset{\substack{\text{Propionic acid} \\ \text{(Main product)}}}{2CH_3\ CH_2\ COOH}$$

A small amount of each acetic and butyric acid is also obtained.

(*ii*) **Haloform reaction**

A carbonyl compound containing at least one methyl group adjacent to >C=O group on treating with a halogen in sodium hydroxide is oxidized to a carboxylic acid. A trihalogen methane derivative is also obtained.

$$\underset{\text{Ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}+3Cl_2+4NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa+\underset{\text{Chloroform}}{CHCl_3}$$
$$+3H_2O+3NaCl$$

This reaction, in fact, involves two stages :

I. **Substitution of three hydrogen atoms of methyl group by halogens :**

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3+3Cl_2+3NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-CCl_3+3H_2O+3NaCl$$

II. **Conversion to trihalomethane** : The bond between the carbon atom of the trihalogen methyl group attached to carbonyl carbon is broken with alkali, *e.g.*,

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CCl_3+NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa+CHCl_3$$

This reaction yields trihalomethanes—chloroform, bromoform and iodoform depending on the halogen used. Since the common name for these compounds is haloform, it is called **haloform reaction**.

Acetaldehyde is the only aldehyde which gives haloform reaction. This reaction serves as a test for the presence of CH_3C- group. For this purpose reaction is carried out with iodine and alkali because a yellow precipitate of iodoform is obtained. This is known as **iodoform test.**

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 + 3OH^- \longrightarrow \underset{\text{Triiodoacetone}}{CI_3COCH_3} + 3H_2O + 3I^-$$

Under the alkaline condition prevailing, the triiodoacetone is broken up into iodoform and sodium acetate.

$$CI_3COCH_3 + NaOH \longrightarrow \underset{\substack{\text{Iodoform}\\ \text{(Triiodomethane)}}}{CHI_3} + \underset{\text{Sodium acetate}}{CH_3COONa}$$

With acetaldehyde :

$$CH_3CHO + 3I_2 + 3OH^- \longrightarrow CI_3CHO + 3H_2O + 3I^-$$

$$\underset{\text{Triiodoacetaldehyde}}{CI_3CHO} + NaOH \longrightarrow \underset{\text{Iodoform}}{CI_3H} + \underset{\text{Sodium formate}}{HCOONa}$$

The same result is obtained by treating acetone with KI and alkaline sodium hypochlorite solution. The hypochlorite oxidizes iodide to iodine and this together with alkali present, produce iodoform from the acetone.

$$NaOCl + 2KI + H_2O \longrightarrow NaCl + I_2 + 2KOH$$

$$CH_3COCH_3 + 3I_2 + 3OH^- \longrightarrow CI_3COCH_3 + 3H_2O + 3I^-$$

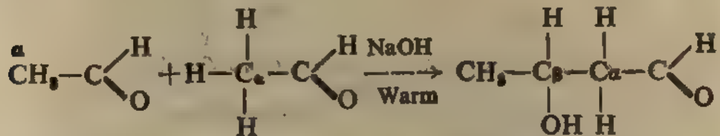
$$CI_3COCH_3 + KOH \longrightarrow \underset{\text{Iodoform}}{CI_3H} + CH_3COOK$$

This reaction is useful for distinguishing methyl ketones from other ketones. It is also used for preparing carboxylic acid with one carbon less than the original methyl ketone.

(*b*) **Reactions involving alkyl group**

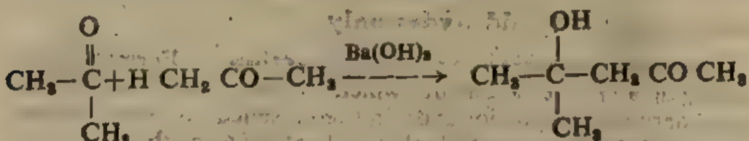
(*i*) **Aldol condensation** : Two molecules of an aldehyde with at least one α-hydrogen atom condense in the presence of dilute alkali (sodium carbonate or hydroxide) to give a β-hydroxy aldehyde. The product obtained from acetaldehyde is known as aldol and the reation is known as aldol condensation. The product has

both an aldehyde and an alcohol group and is a polymer (dimer) rather than a condensation product. It involves the addition of one molecule of aldehyde to the >C=O group of another, coupled with cleavage of—C—H in α-position.



Adol
(3-Hydroxybutanal)

Ketones containing α-hydrogen also undergo aldol condensation to a smaller extent than do aldehydes.



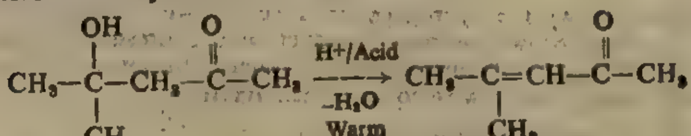
Acetone

Diacetone alcohol
(4-Hydroxy—4-methyl 2-pentanone)

The product (aldol) can be easily dehydrated to get α, β-unsaturated carbonyl compound on warming with an acid.

$$\underset{\text{Aldol}}{CH_3CH(OH)CH_2{-}CHO} \xrightarrow[-H_2O \text{ Warm}]{H^+/\text{Acid}} \underset{\text{Crotonaldehyde}}{CH_3CH{=}CH{-}CHO}$$

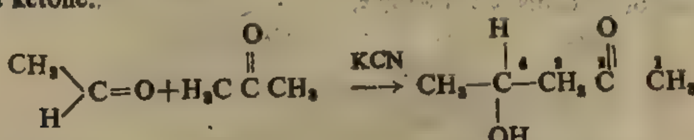
Similarly, diacetone alcohol on heating in the presence of mineral acid dehydrates to mesityl oxide.



Diacetone alcohol

Mesityl oxide

Aldol condensation can also take place between an aldehyde and a ketone.



Acetaldehyde　Acetone　4-Hydroxypentan—2-one

(*ii*) **Halogenation.** Both aldehydes and ketones are readily halogenated. The hydrogen atoms attached to α-carbon atom are replaced by Cl, Br, or I atoms.

$$\underset{\text{Aldehyde}}{R-CH_2-\overset{O}{\overset{\|}{C}}-H}+Cl_2 \xrightarrow[-HCl]{} \underset{\alpha\text{-Chloroaldehyde}}{R-\overset{Cl}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-H}$$

$$R-CH_2-\overset{O}{\overset{\|}{C}}-R'+Br_2 \xrightarrow[-HBr]{} \underset{\alpha\text{-Bromoketone}}{R-\overset{Br}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-R'}$$

All the three α-hydrogen atoms can be substituted by halogen atoms depending on the reaction time and conditions. The halogenation is catalyzed by acids and bases, but occurs with more readily with the latter.

(c) Reaction given by aldehydes only

Cannizzaro reaction (oxidation reaction) : Formaldehyde, benzaldehyde and other aldehydes which do not have α-hydrogen atoms, undergo disproportionation in the presence of concentrated alkali to give a mixture of an alcohol and salt of a carboxylic acid. One molecule of the aldehyde is oxidized at the expense of the other which is reduced.

$$\underset{\text{Formaldehyde}}{2HCHO} \xrightarrow{NaOH} \underset{\text{Methyl alcohol}}{CH_3OH}+\underset{\text{Sodium formate}}{HCOONa}$$

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow{NaOH} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}+\underset{\text{Sodium benzoate}}{C_6H_5COONa}$$

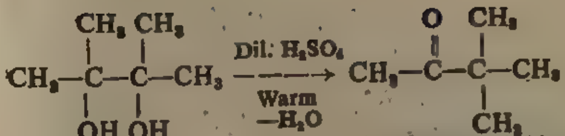
Aldehydes with α-hydrogens on reacting with concentrated alkali form dark brown resinous product which presumbly arise through a series of aldol condensation. Ketones, however, do not form resins when treated with concentrated alkali.

(d) Reaction given by ketones only

Reduction to pinacols : Ketones on reducing with magnesium amalgam and water in neutral or alkaline medium give 1, 2-diols or pinacols. For example,

$$CH_3-\overset{CH_3}{\overset{|}{C}}=O+2[H] \xrightarrow[H_2O]{Mg/Hg} \underset{\substack{\text{2, 3 Dimethyl butane-2, 3-diol} \\ \text{(Pinacol)}}}{CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3}$$

Pinacol on heating with dilute H_2SO_4 undergoes rearrangement and dehydration to form pinacolone (a monketone).



Pinacol → tert-Butyl methyl ketone (Pinacolone)

Some of the important reactions of aldehydes and ketones are summarized in Figs. 8.3 and 8.4 respectivly.

8.3.8 Distinguishing Tests for Aldehydes and Ketone

Reagent/test	*Aldehyde*	*Ketone*
Tollen's reagent	Ag mirror	No Ag mirror
Fehling's solution	Red ppt.	No red ppt.
Schiff's reagent	Pink colour	No pink colour
Phenylhydrazine	Crystalline phenylhydrazone	Crystalline phenylhydrazone

A comparison of aliphatic and aromatic aldehydes

	Ethanal, CH_3CHO	*Benzaldehyde C_6H_5CHO*
Reagent	*Product*	*Product*
$KMnO_4$, acid	CH_3CO_2H	$C_6H_5CO_2H$
$LiAlH_4$ (ethoxyethane)	CH_3CH_2OH	$C_6H_5CH_2OH$
PCl_5 or $SOCl_2$	CH_3CHCl_2	$C_6H_5CHCl_2$
NCN	$CH_3CH(OH)CN$	$C_6H_5CH(OH)CN$
$HaHSO_3$	$CH_3CH(OH)SO_3Na$	$C_6H_5CH(OH)SO_3Na$
$C_6H_5NHNH_2$	$CH_3CH{=}NNHC_6H_5$	$C_6H_5CH{=}NNHC_6H_5$
NH_2OH	$CH_3CH{=}NOH$	$C_6H_5CH{=}NOH$
NaOH(aq)	$CH_3CH(OH)CH_2CHO$	$C_6H_5CH_2OH+C_6H_5CO_2Na$
Cl_2	CCl_3CHO	C_6H_5COCl
Cl_2+Halogen-carrier	—	3-ClC_6H_4CHO
Conc. HNO_3+Conc. H_2SO_4	—	3-$O_2NC_6H_4CHO$
Hot conc. H_2SO_4	—	3-$HO_3SC_6H_4CHO$
Fehling's solution	Red Cu_2O	—
Tollens' reagent	Ag mirror	—
KI, KI, NaClO	CHI_3, iodoform	—
Conc. H_2SO_4	$(C_2H_4O)_3$, paraldehyde	—

8.3.9. Commercially Important Carbonyl Compounds

(*a*) **Methanol (formaldehyde).** HCHO

Formaldehyde can be prepared from methanol by :

(*i*) Dehydrogenation over heated copper at 473 K

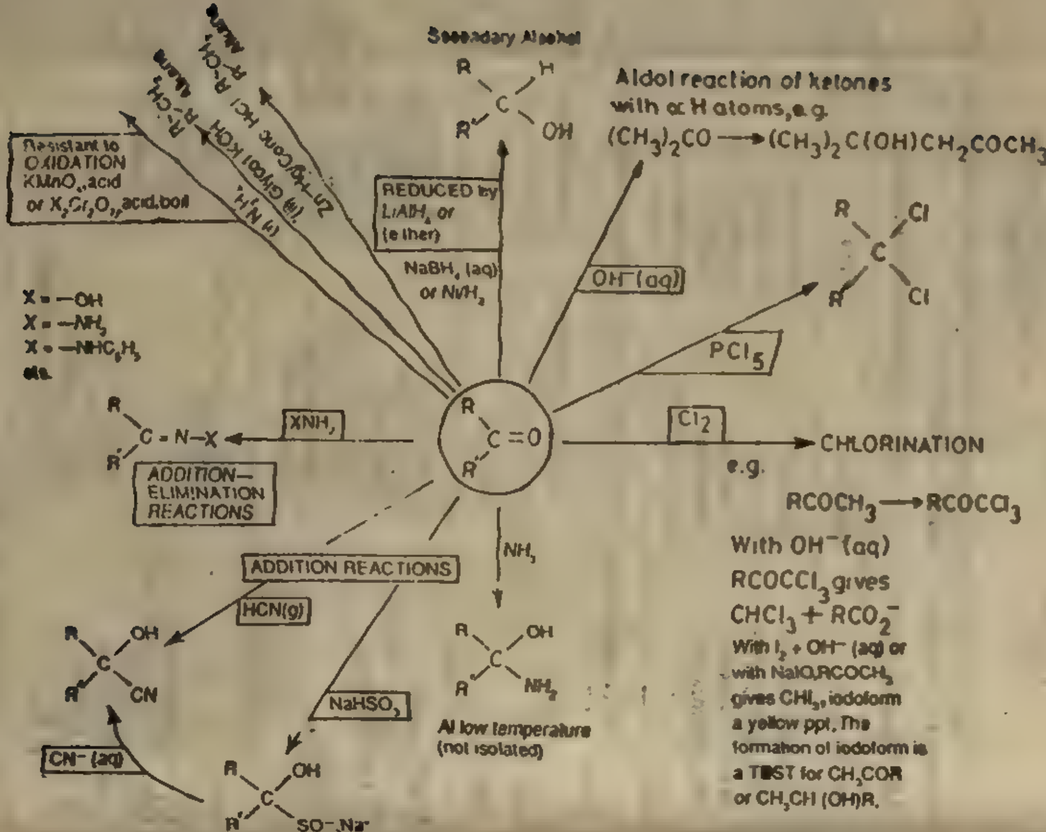


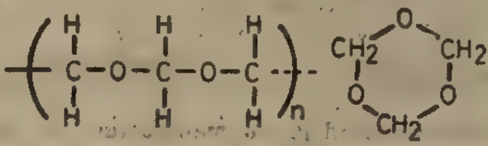
Fig. 8·4 A summary of the reactions of ketones

$$CH_3OH \xrightarrow[573\ K]{Cu} HCHO + H_2$$

(*ii*) Oxidation with controlled amount of air in presence of catalyst (silver ganules or mixture of metal oxides)

$$2CH_3OH + O_2 \xrightarrow[523\text{-}573\ K]{Cu\ or\ Ag} 2HCHO + 2H_2O$$

It is a gas (bp 252 K) and is available as a solution in water (approx. 40%), called formalin. It is also available as solid polymers, paraformaldehyde, $(CH_2O)_n$ and trioxane, $(CH_2O)_3$



Trioxane

$$-\!\!(CH_2O-CH_2O-CH_2O)\!\!-_n$$

Paraformaldehyde

Formaldehyde, when required, can be obtained by heating paraformaldehyde or trioxane.

Formalin is a disinfectant and a preservative for biological samples. It is used in the manufacture of bakelite, resins and other polymers. A typical example is the formation of urea-formaldehyde polymer.

(*b*) **Ethanal (acetaldehyde)**, CH_3CHO.

Acetaldehyde can be prepared from acetylene or from ethanol.

(*i*) From acetylene : Acetylene when passed into dilute sulphuric acid in the presence of $HgSO_4$ forms acetaldehyde.

$$HC{\equiv}CH + H_2O \xrightarrow[HgSO_4]{Dil.\ H_2SO_4} CH_3CHO$$

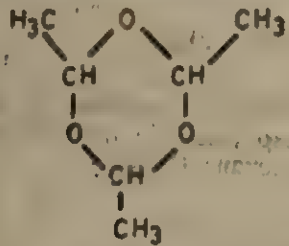
Recently, palladium salts have been used as catalyst in the preparation of acetaldehyde from ethylene.

$$CH_2{=}CH_2 + H_2O \xrightarrow{Pd^{2+}} CH_3CHO$$

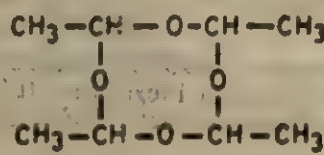
(*ii*) From ethanol : Ethanol is dehydrogenated by passing over heated copper at 573 K,

$$CH_3CH_2OH \xrightarrow{Cu,\ 573\ K} CH_3CHO + H_2$$

Acetaldehyde in the presence of acid can be polymerized to a trimer, paraldehyde or a tetramer, metaldehyde. These yield acetaldehyde on heating with dilute sulphuric acid. The trimer paraldehyde has been used in medicine as a hypnotic.



Paraldehyde

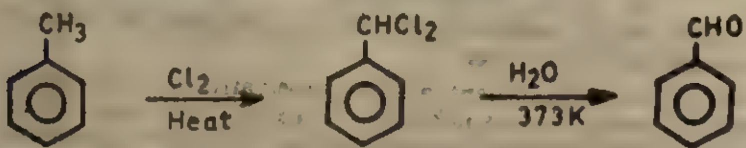


Metaldehyde

Ethanal is mostly used in the manufacture of ethanol. It is also used as an intermediate in the manufacture of a limited range of plastics, resins and drugs.

(*c*) **Benzaldehyde,** C_6H_5CHO.

Benzaldehyde is prepared by side-chain chlorination of toluene to benzal chloride followed by its hydrolysis :



Toluene Benzal chloride Benzaldehyde

It is used in the manufacture of dyes and in perfumery.

(*d*) **Acetone,** CH_3COCH_3.

Acetone is manufactured either from isopropyl alcohol or propylene.

(*i*) By dehydrogenation of isopropyl alcohol vapours by heated copper :

$$\underset{\substack{|\\ OH}}{CH_3CH}-CH_3 \xrightarrow[573\ K]{Cu} \underset{\text{Propanone}}{CH_3-\underset{\substack{\|\\ O}}{C}-CH_3} + H_2$$

(*ii*) By catalytic hydration of propylene, followed by oxidation :

$$CH_3-CH=CH_2 \xrightarrow[\substack{\text{Catalyst}\\ \text{2. [O]}}]{\text{1. Steam}} CH_3-\underset{\substack{\|\\ O}}{C}-CH_3$$

Acetone is widely employed as a solvent and as an intermediate in the manufacture of other organic compounds, such as ethanoic anhydride, trichloromethane, *etc.*

8.3.10. Uses of Aldehydes and Ketones

Ketones with small number of carbon atoms are excellent industrial solvents. Some of the carbonyl compounds are used for producing perfumes and artificial flavours. They are employed as intermediates and starting materials in the manufacture of organic compounds (Fig. 8·5).

8.4. CARBOXYLIC ACIDS

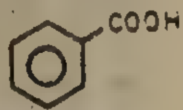
These compounds are characterized by the presence of the carboxyl group $-\overset{\overset{O}{/}}{C}-OH$. The term carboxyl is a combination of the terms, carbonyl $(-\overset{\overset{O}{\|}}{C}-)$ group and hydroxyl $(-OH)$ hence, the name carboxyl group. However, the properties of the carboxyl group are quite distinct from the properties of these two groups.

Compounds which contain one carboxyl attached to an alkyl or aryl group are called monocarboxylic acids. The carboxylic acids are classified as mono-, di-, tri··· or polycarboxylic acids according to the number of carboxyl groups present in them.

The aliphatic monocarboxylic acids are also referred to as fatty acids, as some of the higher members $(C_{12}-C_{18})$ occur in natural fats as esters from which they are obtained by the hydrolysis.

According to the attachment of carboxyl group to alkyl or aryl group, the acids are known as aliphatic or aromatic carboxylic acids respectively.

CH_3CH_2COOH
Propanoic acid
(Aliphatic acid)



Benzoic acid
(Aromatic acid)

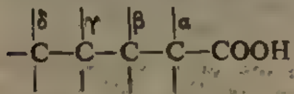
Hydrogen atoms of the alkyl or aryl group may be substituted by some other groups, such as $-OH$, $-NH_2$, $-X$, *etc.* Such acids are known as substituted carboxylic acid.

$X-CH_2COOH$ (Halogen acid) NH_2-CH_2COOH (Amino acid) $HO-CH_2-COOH$ (Hydroxy acid)

The carboxyl group is one of the most widely occurring functional groups in chemistry and bio-chemistry. Not only are carboxylic acids themselves important but the carboxyl group is the parent group of a large family of related compounds.

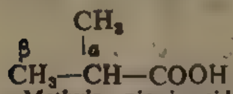
8.4.1. Nomenclature

The carboxylic acids are commonly known by their trivial names which are derived from some natural source of that compound. Thus, formic acid, HCOOH was first obtained by the distillation of ants (from the Latin, formica=ant). Acetic acid, CH_3CO_2H occurs in vinegar (from the Latin, acetum=vinegar). Butyric acid, $CH_3CH_2CH_2COOH$ occurs as an ester in butter. Moreover, the free acid smells like rancid butter (from the Latin, butyrum=butter). Caproic acid (hexanoic acid), $CH_3(CH_2)_3CH_2COOH$ occurs as an ester in goat milk. It smells like goat milk (from the Latin, capper=goat). Octadecanoic acid takes its common name, stearic acid, from the Greek word 'stear', for tallow. In the trivial system, substituents on the chain are designated by Greek letters, *α*, β, γ, *etc.*, starting from the carbon adjacent to the carboxyl group.

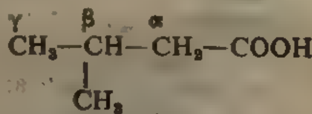


$CH_3—CH_2—COOH$

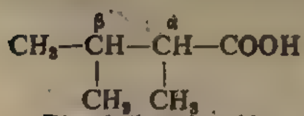
Propionic acid



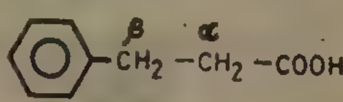
α-Methylpropionic acid
(Isobutyric acid)



β-Methylbutyric acid
(Isovaleric acid)



α, β-Dimethylbutyric acid

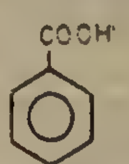


β-Phenylpropionic acid

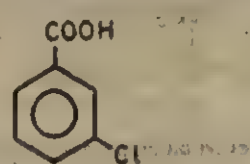
The IUPAC names of carboxylic acids are derived from the corresponding longest straight chain alkane by replacing the last 'e' by 'oic' and adding the word acid. Thus, the acid, CH_3COOH, containing two carbon atoms is called ethanoic ocid. The carboxylic group has to be at one end of the chain and is given number 1.

Acid	Parent hydrocarbon	Trivial name	IUPAC name
HCOOH	H CH_3	Formic acid	Methanoic acid
CH_3COOH	CH_3CH_3	Acetic acid	Ethanoic acid
CH_3CH_2COOH	$CH_3CH_2CH_3$	Propionic acid	Propanoic acid
$CH_3(CH_2)_2COOH$	$CH_3CH_2CH_2CH_3$	Butyric acid	Butanoic acid
$\overset{3}{C}H_3\overset{2}{C}H(CH_3)\overset{1}{C}OOH$	$CH_3CH(CH_3)CH_3$	Isobutyric acid (α-Methyl propionic acid)	2-Methylpropanoic acid
$\overset{4}{C}H_3\overset{3}{C}H(CH_3)\overset{2}{C}H_2\overset{1}{C}OOH$	$CH_3CH(CH_3)CH_2CH_3$	Isovaleric acid (β-Methylbutyric acid)	3-Methylbutanoic acid
$\overset{4}{C}H_3\overset{3}{C}H(CH_3)\overset{2}{C}H(CH_3)\overset{1}{C}OOH$	$CH_3CH(CH_3)CH(CH_3)CH_3$	α, β-Dimethyl butyric acid	2, 3-Dimethyl-butanoic acid
$Br\overset{3}{C}H_2\overset{2}{C}H(CH_3)\overset{1}{C}OOH$	$CH_3CH(CH_3)CH_3$	β-Bromo-α-methyl propionic acid	3-Bromo-2-methyl-propanoic acid

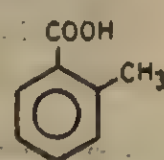
The names of the aromatic acids are usually derived from the first benzoic acid, C_6H_5COOH, which is the parent acid.



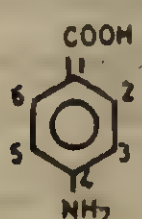
Benzoic acid



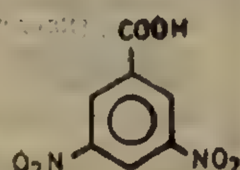
m-Chlorobenzoic acid or 3-Chlorobenzoic acid



o-Methylbenzoic acid or o-Toluic acid



p-Aminobenzoic acid
4-Aminobenzoic acid



3,5-Dinitrobenzoic acid

8.4.2. Isomerism

Like any other organic derivatives such as alcohols, alkyl halides, aldehydes and ketones, carboxylic acids show both **position and chain isomerism**. For example, a carboxylic acid with molecular formula, $C_6H_{12}O_2$ represents the following chain isomers of carboxylic acid :

(*i*) $CH_3CH_2CH_2CH_2CH_2COOH$
Hexanoic acid

(*ii*) $\begin{array}{l} \qquad\qquad\qquad\quad CH_3 \\ \qquad\qquad\qquad\quad \,| \\ CH_3CH_2CH_2CH{-}COOH_3 \end{array}$
2-Methyl pentanoic acid

(*iii*) $\begin{array}{l} \qquad\qquad\quad\;\; CH_2CH_3 \\ \qquad\qquad\quad\;\; | \\ CH_3{-}CH_2{-}CH\ COOH \end{array}$
2-Ethyl butanoic acid

(*iv*) $\begin{array}{l} \qquad\;\; CH_3 \\ \qquad\;\; | \\ CH_3{-}CH{-}CH_2{-}CH_2{-}COOH \end{array}$
4-Methyl pentanoic acid

(*v*) $\begin{array}{l} \qquad\;\; CH_3 \\ \qquad\;\;\; | \\ CH_3{-}C{-}CH_2{-}COOH \\ \qquad\;\;\; | \\ \qquad\;\; CH_3 \end{array}$
3, 3-Dimethyl butanoic acid

(*vi*) $\begin{array}{l} \qquad\qquad\quad CH_3 \\ \qquad\qquad\quad\; | \\ CH_3{-}CH_2{-}CH{-}COOH \\ \qquad\qquad\quad\; | \\ \qquad\qquad\quad CH_3 \end{array}$
2, 2-Dimethyl butanoic acid

Carboxylic acids (*i*), (*ii*) and (*iii*) also exhibit position isomerism.

Carboxylic acids also show functional isomerism with esters containing the same number of carbon atoms. For example : Propionic acid is isomeric with methyl acetate.

CH_3CH_2COOH Propionic acid	CH_3COOCH_3 Methyl acetate

Butyric acid is isomeric both with methyl propionate and ethyl acetate.

$CH_3CH_2CH_2COOH$ Butyric acid	$CH_3CH_2COOCH_3$ Methyl propanoate	$CH_3COOCH_2CH_3$ Ethyl acetate

8.4.3. Preparation of Carboxylic Acids

(*i*) **By hydrolysis of cyanides (nitriles).** Alkyl cyanides, prepared from alkyl halides are hydrolyzed to carboxylic acids.

$$\underset{\text{Alkyl halide}}{RX} \xrightarrow{KCN} \underset{\text{Alkyl cyanide}}{R{-}C{\equiv}N} \xrightarrow{+H_2O} \underset{\text{Amide}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2} \xrightarrow{H_2O} \underset{\text{Ammonium carboxylate}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-NH_4^+}$$

The hydrolysis is catalyzed both by acids and alkalis on boiling. When acid is used the ammonium carboxylate formed in the reaction gives free carboxylic acid and amonium salt of the acid used.

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONH_4 \xrightarrow{+HCl} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + NH_4Cl$$

When alkali is used for the purpose sodium or potassium carboxylate and ammonia acid produced. The carboxylate salt on further hydrolysis gives carboxylic acid.

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONH_4 \xrightarrow{+NaOH} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONa + NH_3 + H_2O$$

$$\downarrow H_2O$$

$$\underset{\text{Carboxylic acid}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}$$

For example :

$$\underset{\text{Ethyl cyanide}}{CH_3CH_2CN} + 2H_2O + HCl \longrightarrow \underset{\text{Propionic acid}}{CH_3CH_2COOH} + NH_4Cl$$

This method provides a carboxylic acid containing one carbon atom more than in the original alkyl halide.

(*ii*) **From Grignard reagents (Carbonation of Grignard reagent)** : If CO_2 is bubbled through an ethereal solution of a Grignard reagent or the ethereal solution of the Grignard reagent is added to powdered solid CO_2 (dry ice) suspended in ether, an addition product is formed. On decomposition with mineral acid, the addition product yields the free carboxylic acid.

$$\underset{\text{Grignard reagent}}{R{-}MgX} + CO_2 \longrightarrow \underset{\text{Addition compound}}{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O\,MgX} \xrightarrow{+HCl/H_2O} \underset{\text{Carboxylic acid}}{R{-}COOH} + Mg\begin{smallmatrix} X \\ Cl \end{smallmatrix}$$

For example,

$$\underset{\text{Grignard reagent}}{CH_3MgBr} + CO_2 \longrightarrow CH_3COO\,Mg\,Br \xrightarrow{+HCl/H_2O} \underset{\text{Acetic acid}}{CH_3COOH} + Mg\begin{smallmatrix} Br \\ Cl \end{smallmatrix}$$

Organolithium compounds can also be used to get carboxylic acid.

It may be noted that, this method also provides a carboxylic acid with one carbon atom more than in the original organometallic compound.

(*iii*) **By oxidation of aldehydes and alcohols**. We already know that primary alcohols can be oxidized to aldehydes which on further oxidation yield carboxylic acids. The usual oxidizing agents used are potassium permanganate or potassium dichromate in sulphuric acid. Aromatic acids may also be prepared by this method as well as dicarboxylic acids from their corresponding diols or dialdehydes.

$$\underset{\text{Alcohol}}{R-CH_2-OH} \xrightarrow{[O]} \underset{\text{Aldehyde}}{RCHO} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{R-C\begin{matrix} \nearrow O \\ \searrow OH \end{matrix}}$$

For example :

$$\underset{\text{Benzylalcohol}}{C_6H_5CH_2OH} \xrightarrow{[O]} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5\,COOH}$$

Aldehydes may also be oxidized by milder oxidizing agents, *e.g.*, Tollen's reagent, *etc.*

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{\text{Tollen's reagent}} \underset{\text{Acid}}{R-COOH}$$

For example :

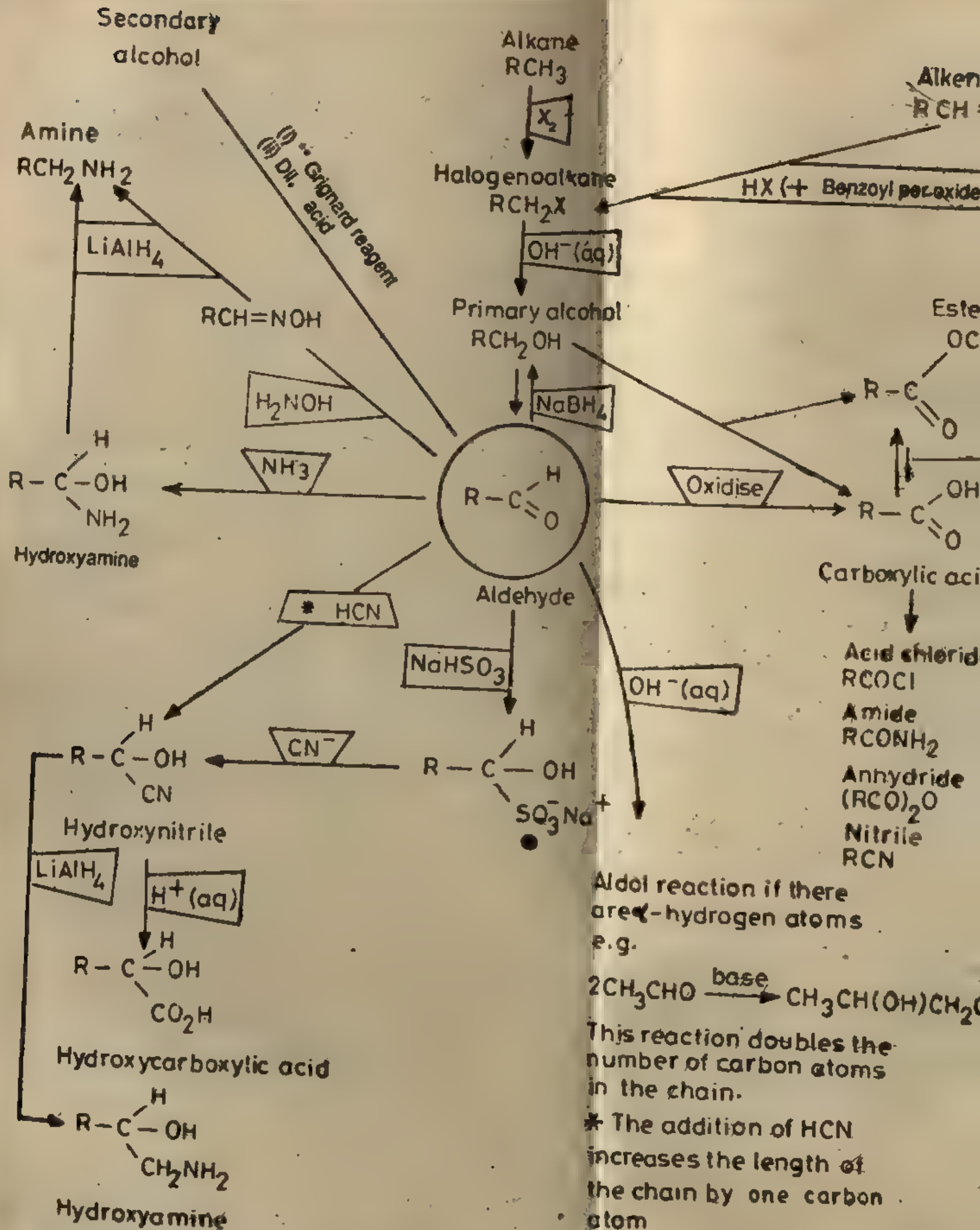
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{\text{Tollen's reagent}} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{\text{Tollen's reagent}} \underset{\text{Acetic acid}}{CH_3COOH}$$

Methyl ketones can be oxidized to the lower carboxylic acids using sodium hypoiodite solution :

$$\underset{\text{Ethyl methyl ketone}}{CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \xrightarrow{NaOI/OH^-} \underset{\text{Propanoic acid}}{CH_3-CH_2-CO_2H} + CHI_3$$

It is interesting to note that by using the above methods primary alcohols may be converted to carboxylic acids containing



Aldol reaction if there are α-hydrogen atoms e.g.

$$2CH_3CHO \xrightarrow{\text{base}} CH_3CH(OH)CH_2C$$

This reaction doubles the number of carbon atoms in the chain.

* The addition of HCN increases the length of the chain by one carbon atom

● With HCHO gives primary alcohol, RCH_2OH with one extra atom

Fig. 8.5 Aldehydes in the preparation of other classes of compounds

the same number of carbon atoms or stepped up to a higher carboxylic acid :

$$RCH_2OH \xrightarrow[H_2SO_4]{KMnO_4} RCHO \longrightarrow RCOOH \text{ (Same no. of C-atoms)}$$

$$\downarrow PCl_5$$

$$RCH_2Cl \xrightarrow{KCN} RCH_2CN \xrightarrow{H^+} RCH_2COOH$$

$$\downarrow \text{Mg/Ether}$$

$$RCH_2MgCl \xrightarrow[(ii)\ H^+]{(i)\ CO_2} RCH_2COOH$$

Refer : Preparation method (*i*)

(Acids with one more C-atom)

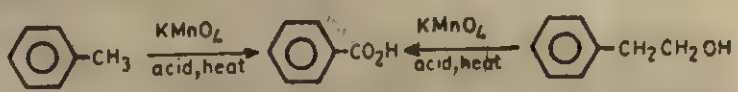
Refer : Preparation method (*ii*)

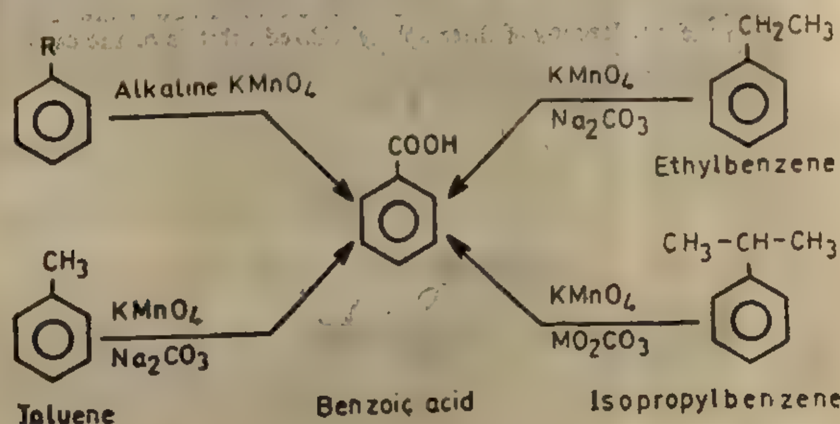
Substitution of a nitrile group and reduction increases the number of C atoms in the chain.

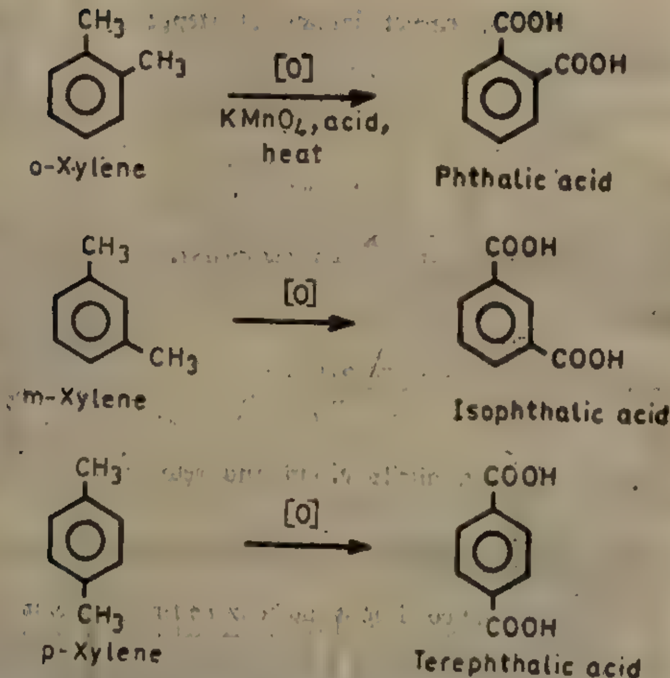
8.4.4. Preparation of Aromatic Carboxylic Acids by Oxidation of Alkyl Benzenes

Under oxidizing conditions the benzene ring is comparatively stable to oxidation and any side chains are oxidized irrespective of the size of a —COOH group. Thus, toluene, ethyl benzene, in fact, any monoalkyl benzene in oxidized only to benzoic acid.

Strong oxidizing agents like alkaline potassium permaganate, acidified potassium dichromate or dilute nitric acid are used for this purpose. Industrially, air is used as the oxidizing agent.







Some of the methods of preparing benzoic acid are given in Fig. 8·6.

8.4.5. Nature of the Carboxyl Group

The carbon atom of the $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ is sp^2 hybridized and is joined to three σ-bonds which including carbon lie in a plane making an angle of 120° with one another. These three σ-bonds are derived from the overlapping of three sp^2 hybridized orbitals of the carboxylic carbon with two sp^2 orbitals of two oxygen atoms and one sp^3 hybridized orbital of the alkyl group.

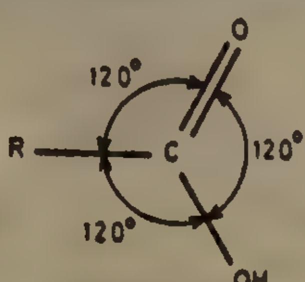
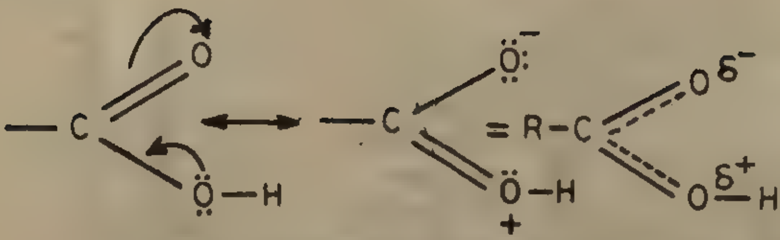


Fig. 8.6. Preparation of benzoic acid

The >C=O group has a double bond between carbon and oxygen and because of difference in electronegativity between these two, the π-electrons are not equally shared. The electron cloud is polarized towards the oxygen. In this process, —OH bond is weakened as >C=O group tends to pull electrons on oxygen in $-\ddot{\underset{..}{O}}H$ towards itself. Hence the π-electrons are partially delocalized between carbon and one oxygen on the one hand and the carbon and second oxygen on the other hand. Thus, the carboxyl group is a resonance hybrid of the following two structures.

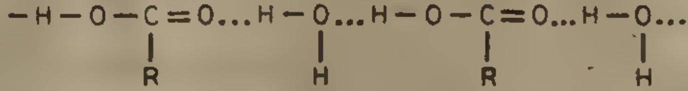


The structure has separated charges.

8.4.6. Physical Properties

The first three monocarboxylic acids are colourless liquids with pungent smell. The next six acids (C_4 to C_9) are oily liquids with an odour of rancid butter, while the higher ones are colourless, odourless wax-like solids. The aromatic acids do not have any smell and are colourless crystalline solids. Carboxylic acids are polar compounds and can form hydrogen bonds, which is reflected in many of their physical properties.

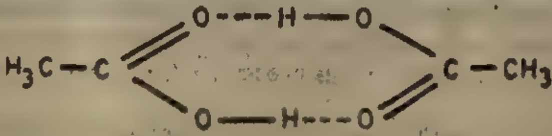
Thus, lower aliphatic acids (upto C_4) are miscible with water but as the size of the alkyl group (molecular masses) increases, the solubility decreases. Thus, higher aliphatic members and aromatic acids are nearly insoluble in cold water. However, carboxylic acids (aromatic and aliphatic) are soluble in organic solvents such as alcohol, ether, benzene, *etc.*



Hydrogen bonding between water and carboxylic acid.

Carboxylic acids have a higher boiling point than alcohols of comparable molecular masses (acetic acid, mol mass=60, bp 391K; *n*-propyl alcohol, mol mass=60, bp 370K).

This is because of the greater degree of hydrogen bonding in carboxylic acids than in alcohols. In fact these exist as dimers, due to intermolecular hydrogen bonding :



Acetic acid dimer

The existence of a dimer has been proved in solution of acetic acid in benzene ; when the observed colligative properties work out to a molecular mass of 120, instead of 60.

Odd and even series of acids. If the melting points of aliphatic acids are plotted against the number of carbon atoms present (Fig. 8·7) it is observed that the melting point of an acid having an odd number of carbon atoms is less than one with even number of carbon atoms immediately before and after it. X-ray diffraction studies have shown, that even number acids have carboxyl and terminal methyl groups on the opposite sides of the zig-zag carbon chain and fit better in the crystal lattice (*i.e.*, have greater van der Waals forces). The odd number acids have carboxyl and terminal methyl groups on the same side and do not fit as well in the crystal lattice. The even number acids, therefore, have higher melting points. This kind of effect is also observed in the melting points of normal paraffins, dibasic acids, *etc.*

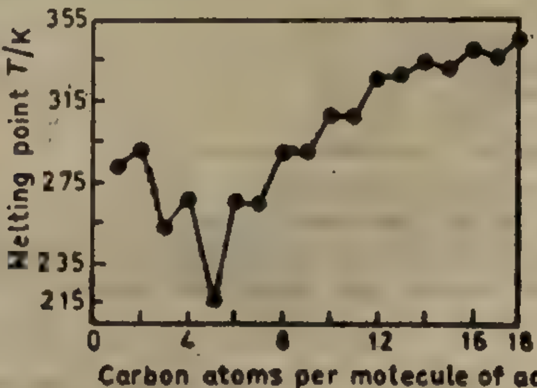


Fig. 8.7. Variation in the melting points of aliphatic acids with the number of carbon atoms in the molecule

8.4.7. Chemical Properties and Reactions

Acidity. Next to mineral acids, carboxylic acids are the most acidic amongst the organic compounds. In aqueous solution they furnish hydronium and carboxylate ions.

$$\underset{\text{Carboxylic acid}}{RCOOH} + H_2O \longrightarrow \underset{\text{Carboxylate ion}}{RCOO^-} + \underset{\text{Hydronium ion}}{H_3O^+}$$

At equilibrium, the concentration of the components are related by the expression

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

the equilibrium constant, K_a is called acidity or dissociation constant. The larger the value of K_a, the stronger is the acid. Generally the acid strength is expressed in terms of pK_a ($pK_a = -\log K_a$). Table 8·2 lists the K_a and pK_a values for a number of acids.

TABLE 8·2. K_a and pK_a values of some organic acids

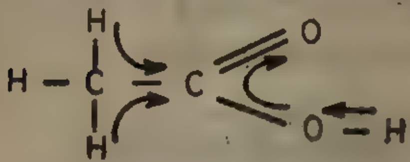
Acid	$K_a \times 10^{-5}$ at 398 K	pK_a
HCOOH	17·7	3·75
CH_3COOH	1·75	4·76
CH_3CH_2COOH	1·3	4·87
$ClCH_2COOH$	136	2·87
$Cl_2CHCOOH$	5530	1·26
Cl_3CCOOH	23300	0·64
FCH_2COOH	260	2·66
$BrCH_2COOH$	125	2·90
ICH_2COOH	67	3·17
$HOCH_2COOH$		3·83
$COOH-CH_2COOH$	150	2·83
$CH_3CH_2CH_2COOH$	1·6	4·82
C_6H_5COOH	6·5	4·20

The strength of organic acids depends on :

(*i*) the ease of ionization of the O—H link.

(*ii*) the stability of the resulting anion.

The oxygen atom of >C=O group tends to pull electrons towards itself thus weakening O—H and C—H bonds.



This enhances the ionization of the O—H bond.

Both the acid and carboxylate anion are resonance hybrids of the followings structures :

(I) (II)

Non-equivalent

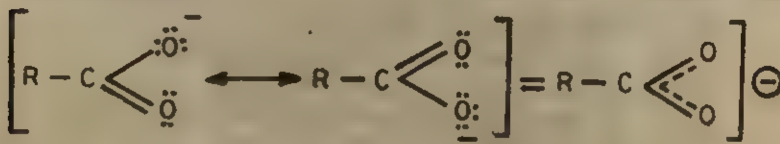
Structures (I) and (II) are non-equivalent, differ significantly in energy and do not make equal contribution to the resonance hybrid. In the resonance hybrid, the oxygen of O—H group carries +ve

charge. Owing to the +ve charge, the electron pair of the O—H group is displaced towards oxygen, thereby facilitating the release of proton with the formation of carboxylate ion. Thus

$$[R-\overset{\overset{\ddot{O}:}{\|}}{C}-\ddot{O}-H \leftrightarrow R-\overset{\overset{:\ddot{O}:^{-}}{|}}{C}=\overset{+}{\ddot{O}}-H] \rightleftharpoons H^{+} + \underset{\text{Carboxylate ion}}{RCOO^{-}}$$

It explains the acidic nature of the carboxyl group.

The negative charge on the carboxylate ion is spread equally over the two oxygen atoms. The ion is a resonance hybrid of two equivalent structures (III) and (IV) which contribute equally to the overall structure.



(III) (IV)

Thus the resonance energy of carboxylate ion is much higher than that of acid itself. Carboxylic acids will, therefore, dissociate to more stabilised carboxylate ions and release H^+ ions.

It is now clear that if the same charge (positive or negative) on an ion is increased, it becomes less stable, *i.e.*, with increasing negative charge, the carboxylate ion is destabilised.

Thus, any substituent, that stablises the carboxylate ion more, would facilitate the release of protons and increase the acidity. On the other hand, any substituent that destabilises the carboxylate ion would decrease the acidity. Thus the electron withdrawing (—I) substituents (Cl, NO_2, CN, OH, NH_2, *etc.*) would decrease the negative charge of $-\overset{\diagup O}{C}-O$ ion and would stabilise it and thus enhance the acid strength. On the other hand, a electron donating (+I) substituents (alkyl, *etc.*) would increase the intensity of negative charge on the $-\overset{\diagup O}{C}-O$ ion and thus destabilise it, consequently the carboxylic acid becomes less acidic. For example :

$$\underleftarrow{FCH_2COOH > ClCH_2COOH > Br\,CH_2COOH > I\,CH_2COOH}$$

Acidity increases with increasing electronegativity of halogen.

$$\underleftarrow{Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH}$$

Acidity increases with increasing number of Cl atoms.

$$CH_3CH_2CH_2COOH > CH_3CH_2COOH > CH_3COOH > HCOOH$$

$\longleftarrow$

Acidity decreases with increasing size of alkyl group.

$$ClCH_2CH_2CH_2COOH > CH_3\underset{\displaystyle Cl}{\underset{|}{C}H}CH_2COOH > CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}H}COOH$$

$\longleftarrow$

Acidity decreases with increasing distance of Cl atom from —COOH group.

(a) Reactions involving removal of proton from —COOH

(i) **Acidic properties** : The acid strength gradually decreases among the homologues as the relative molecular mass increases. These acids affect indicators, and

(a) neu ralize alkalis forming salts :

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

(b) ammonium salts are formed with amonia :

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{Ammonium acetate}}{CH_3COO^- \, NH_4^+}$$

(c) liberate carbon dioxide from carbonates :

$$2CH_3COOH + Na_2CO_3 \rightarrow CO_2 + H_2O + 2CH_3COONa$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaHCO_3 \rightarrow CO_2 + H_2O + \underset{\text{Sodium acetate}}{CH_3COONa}$$

(d) salt formation occurs with a organic base :

$$CH_3COOH + N(C_2H_5)_3 \longrightarrow \underset{\text{Triethyl ammonium acetate}}{CH_3COO^- \, \overset{+}{H}N(C_2H_5)_3}$$

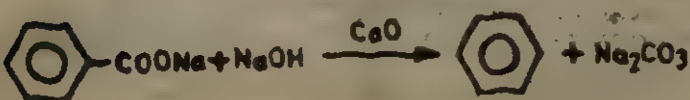
(e) evolve hydrogen during reaction with very reactive metals such as zinc, magnesium, *etc.*

$$\underset{\text{Acetic acid}}{2CH_3COOH} + Mg \longrightarrow \underset{\text{Magnesium acetate}}{(CH_3COO)_2Mg} + H_2$$

The above reactions pertain to the removal of proton from —OH by a base.

(ii) **Decarboxylation** : The removal of COO^- is termed decarboxylation. Salts of carboxylic acids undergo decarboxylation under a variety of conditions. Thus, the sodium salt of acetic acid when heated with soda lime (a mixture of NaOH and CaO) yields methane.

$$\underset{\text{Sodium acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa} + NaOH \xrightarrow{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$



If sodium acetate is electrolyzed (Kolbe method for perparation of alkanes), then enthane is obtained.

$$\underset{\text{Sodium acetate}}{CH_3COO^-Na^+} \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2CO_2 + 2NaOH + H_2$$

$$2CH_3COONa \rightleftharpoons 2CH_3COO^- + 2Na^+$$

$$-2e^- \downarrow \qquad\qquad \downarrow +2e^-$$

$$\underbrace{C_2H_6(g) + 2CO_2(g) \leftarrow 2CH_3COO}_{\text{At anode}} \qquad \underbrace{2Na \xrightarrow{2H_2O} 2NaOH(aq) + H_2(g)}_{\text{At cathode}}$$

Calcium salts of carboxylic acids (except formic acid) on heating yield ketones.

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{Heat}} \underset{\text{Acetone}}{CH_3COCH_3} + CaCO_3$$

However, if a mixture of calcium salt of a carboxylic acid and calcium formate is heated, an aldehyde is obtained.

$$\underset{\substack{\text{Calcium}\\\text{acetate}}}{(CH_3COO)_2\,Ca} + \underset{\substack{\text{Calcium}\\\text{formate}}}{(HCOO)_2\,Ca} \longrightarrow \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2CaCO_3$$

All dicarboxylic acids, containing the two carboxyl groups attached to the same carbon atom are decarboxylated simply on heating :

$$\underset{\text{Malonic acid}}{CH_2(COOH)_2} \xrightarrow{415\text{-}435\text{ K}} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

Ammonium salts when heated alone produce the corresponding amides with the liberation of a water molecule.

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

Ammonium acetate on heating with P_2O_5 gives cyanides.

$$CH_3COONH_4 \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Methyl cyanide}}{CH_3{-}C{\equiv}N} + 2H_2O$$

(*b*) Reactions of the carboxyl carbon (attack of nucleophile)

(*iii*) **Conversion to anhydrides** : A carboxylic acid on heating with phosphorus pentoxide gives anhydride.

$$\underset{\text{Acetic acid}}{2CH_3\,COOH} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

A carboxylic acid on treating with corresponding acid chloride in the presence of pyridine also forms anhydride.

$$\underset{\text{Acid}}{RCOOH} + \underset{\substack{\text{Acid}\\\text{chloride}}}{RCOCl} \xrightarrow[-HCl]{\text{Pyridine}} \underset{\text{Acid anhydride}}{(RCO)_2O}$$

(*iv*) **Conversion to esters :** A carboxylic acid on treating with alcohol in the presence of concentrated H_2SO_4 (catalyst) or dry hydrogen chloride forms ester. This reaction known as esterification is a reversible process (Mechanism will be discussed under esters).

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

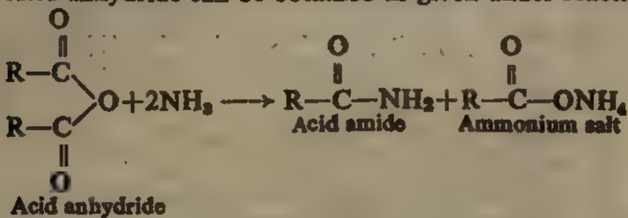
(*v*) **Conversion to amide :** Acid chlorides and acid anhydrides react vigorously with ammonia to form the amide.

Carboxylic acids can be converted to their corresponding acid halides by reaction with phosporous halides (PCl_3, PCl_5, PBr_3) or thionyl chloride.

$$\underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow{PCl_5} R-\overset{\overset{O}{\|}}{C}-Cl + POCl_3 + HCl$$

$$\underset{\text{Acid chloride}}{R-\overset{\overset{O}{\|}}{C}-Cl} + 2NH_3 \longrightarrow \underset{\text{Acid amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} + NH_4Cl$$

Acid anhydride can be obtained as given under reaction (*iii*).



For example :

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Ammonium acetate}}{CH_3COONH_4}$$

Ammonium salt of carboxylic acid on heating also gives an acid amide [Ref. reactions of salts of carboxylic acid under decarboxylation p. 405.]

(*c*) **Reduction of >C= group**

Carboxylic acids and their functional derivatives are reduced directly to the corresponding primary alcohol by lithium aluminium hydride.

$$R-COOH \xrightarrow{LiAlH_4} R-CH_2OH$$

For example :

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

(*d*) **α-Halogenation of aliphatic acids**

In this reaction of carboxylic acids with chlorine or bromine in the presence of a small amount of phosphorus, the α-hydrogens are replaced successively to yield α-halogenated acids.

$$\overset{\beta}{C}H_3\overset{\alpha}{C}H_2COOH \xrightarrow{Br_2/P} CH_3\underset{\underset{Br}{|}}{C}H{-}COOH \xrightarrow{Br_2/P} CH_3{-}\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}{-}COOH$$

Bromo propioinc acid — Dibromopropionic acid

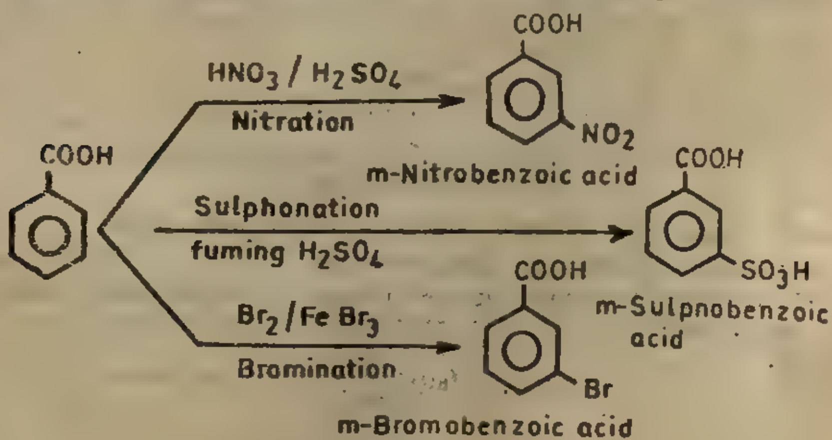
This reaction is known as **Hell-Volhard-Zelinski** (HVR) reaction. This reaction has a great synthetic importance as the halogen atom can be substituted by a number of other groups giving valuable products.

For example :

$$RCH_2\underset{\underset{Br}{|}}{C}HCOOH \rightarrow \begin{cases} \xrightarrow{NaOH\ (aq)} RCH_2\underset{\underset{OH}{|}}{C}HCOOH & (\alpha\text{-Hydroxy acid}) \\ \xrightarrow{NH_3} RCH_2\underset{\underset{NH_2}{|}}{C}HCOOH & (\alpha\text{-Amino acid}) \\ \xrightarrow{\text{Alcoholic KOH}} RCH{=}CHCOOH & (\alpha,\beta\text{-Unsaturated acid}) \\ \xrightarrow{KCN} RCH_2\underset{\underset{CN}{|}}{C}HCOOH \xrightarrow{H^+} RCH_2\underset{\underset{COOH}{|}}{C}HCOOH & (\text{Dicarboxylic acid}) \end{cases}$$

(*e*) **Ring substitution in aromatic acids**

The carboxyl group is an electron withdrawing group and, when present in the benzene nucleus, *e.g.*, in benzoic acid, it deactivates the ortho- and para- positions, and therefore, electrophilic substitu-



tion (nitration, sulphonation, halogenation) takes place at the meta- position.

Methods of preparing carboxylic acids and their important reactions are given in Fig. 8·8.

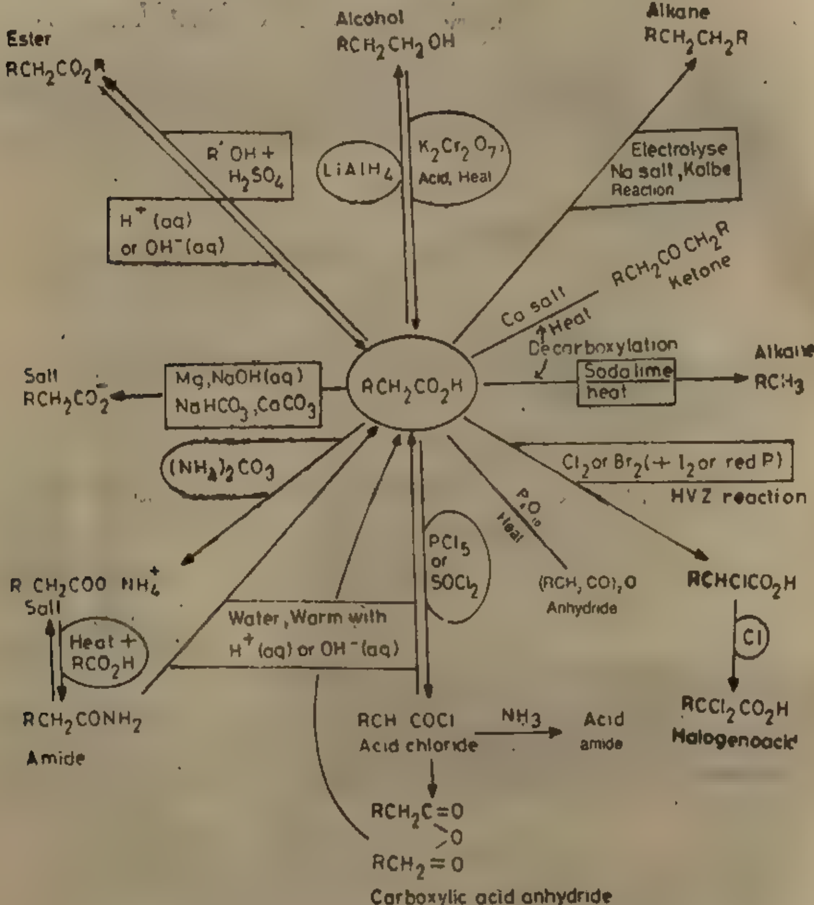


Fig. 8.8. Methods of preparing carboxylic acids and their reactions.

8.4.8. Some Commercially Important Carboxylic Acids

Methanoic acid (formic acid), HCOOH

Formic acid is manufactured by reacting carbon monoxide and sodium hydroxide under pressure at 473K.

$$CO + NaOH\,(aq) \xrightarrow[10\ atm]{473K} HCOONa$$

Dilute sulphuric acid is added to a slurry of crushed sodium salt and the contents are heated to distil the formic acid.

$$HCOONa + H_2SO_4 \xrightarrow{\text{Heat}} HCOOH + NaHSO_4$$

Formic acid is irritating to the eyes, nose, *etc.* It burns the skin and causes blisters. It has a strong antiseptic action.

It is used in rubber, leather and electroplating industries.

It has medicinal value. It is used for storing and generating carbon dioxide.

Ethanoic acid (Acetic acid) CH_3COOH

A dilute (~10%) solution of acetic acid is called vinegar. Vinegar is still manufactured by the ancient method of fermentation of ethyl alcohol in the presence of a special bacteria, bacterium aceti (acetobacter) and air.

The dilute solution can be concentrated by distillation to get pure acid known as glacial acetic acid.

$$CH_3CH_2OH + O_2 \xrightarrow{\text{Acetobacter}} CH_3COOH + H_2O$$

In the pure form it is manufactured.

(*i*) by hydration of acetylene to acetaldehyde followed by oxidation to acetic acid.

$$CH{\equiv}CH \xrightarrow[\text{HgSO}_4]{\text{Dilute H}_2\text{SO}_4} CH_3CHO \xrightarrow[\text{Mn}^{2+}]{O_2} CH_3COOH$$

(*ii*) by dehydrogenation of ethyl alcohol to acetaldehyde followed by oxidation. Alcohol vapours when passed over copper catalyst at 570K give acetaldehyde which, in turn, on oxidation gives ethanoic acid.

$$CH_3CH_2OH \xrightarrow{\text{Cu, 570K}} CH_3CHO \xrightarrow[\text{Mn}^{2+}]{O_2} CH_3COOH$$

(*iii*) by carboxylation of methanol in the presence of rhodium catalyst.

$$CH_3CHO + CO \xrightarrow{\text{Rh}} CH_3COOH$$

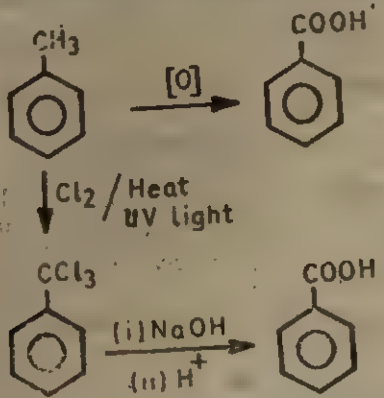
Anhydrous acid has corrosive action on the skin and causes blisters.

Ethanoic acid is used, (*i*) in the manufacture of rayon, (*ii*) in the industries of rubber, plastics and silk, (*iii*) in the manufacture of acetates, acetone, esters, *etc.*, (*iv*) in medicines, *etc.*, (*v*) as solvent, (*vi*) as vinegar in cooking.

Higher carboxylic acids containing even number of carbon atoms (six to eighteen) can be obtained by the hydrolysis of vegetable fats.

Benzoic acid (C_6H_5COOH)

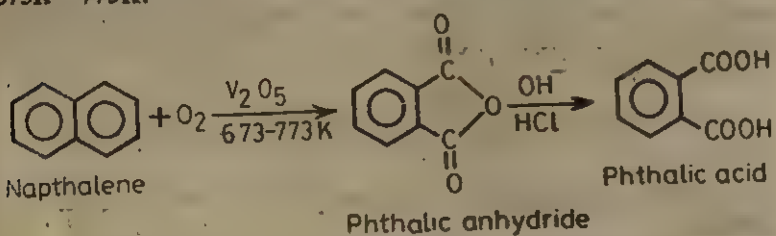
This important aromatic carboxylic acid is manufactured from toluene either by oxidation or chlorination followed by hydrolysis :



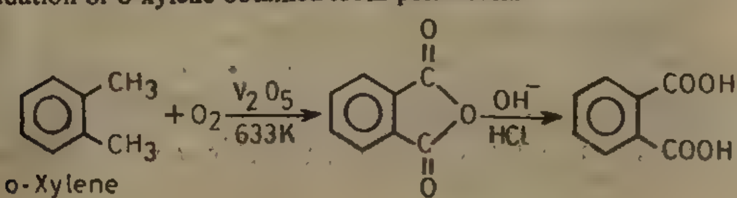
Benzoic acid is used : (*i*) in perfume industry, (*ii*) in dye industry for making aniline blue, (*iii*) as salt in preserving food, (*iv*) in medicine as urinary antiseptic and in the vapour form for disinfecting bronchial tubes.

Phthalic acid (benzene, 1, 2- di carboxylic acid), C_6H_4 COOH

Phthalic acid is manufactured by passing a mixture of naphthalene vapour and air, over vanadium pentoxide as catalyst at 673K—773K.



By another but a newer method, it is produced by thecatalytic oxidation of o-xylene obtained from petroleum.



Phathalic acid or its derivatives are used : (*i*) in producing dyes, (*ii*) as esters needed as plasticisers for synthetic resins, (*iii*) as diethyl derivative in perfume industry.

Terephthalic acid (benzene, 1, 4–dicarboxylic acid)

Terephthalic acid is produced by the catalytic oxidation of 1, 4–dimethyl benzene.

Terephthalic acid is used as basic raw material for manufacturing polyester.

8.5. DERIVATIVES OF CARBOXYLIC ACIDS

The hydroxyl group —OH, in a carboxylic acid can be replaced by other functional groups. These compounds may be given by the general formula

$$R-\overset{\overset{\large O}{\|}}{C}-Y$$

Since all of them contain the acyl group (RCO—), they are also known as acyl derivatives. When Y is one of the halogen atoms, we get acyl halides or acid halides, when Y is an amino group we get acid amides ($R-\overset{\overset{O}{\|}}{C}-NH_2$). Other functional derivatives of acids are esters (R—CO—OR′) and acid anhydrides, $(RCO)_2O$.

8.5.1. Acyl Halides

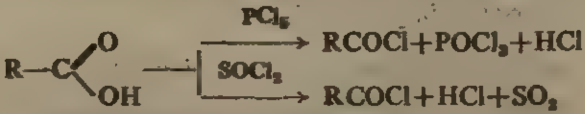
Acyl halides are also termed as acid halides. Of all the acyl halides, the chlorides are well characterized. They are among the most reactive acyl compounds. In naming them by the common system or the IUPAC system, the terminal '-ic acid' of the name of the acid is changed to '-yl chloride'. Some examples are given in Table 8.3.

TABLE 8·3. Names of some acyl chlorides

Acid chloride	*Parent acid*	*Common name*	*IUPAC name*
CH_3COCl	CH_3COOH	Acetyl chloride	Ethanoyl chloride
CH_3CH_2COCl	CH_3CH_2COOH	Propionyl chloride	Propanoyl chloride
$CH_3(CH_2)_2COCl$	$CH_3(CH_2)_2COOH$	*n*-Butyryl chloride	Butanoyl chloride
C_6H_5COCl	C_6H_5COOH	Benzoyl chloride	Benzoyl chloride

Preparation. Aliphatic acid chlorides are prepared from carboxylic acids by reagents which replace an —OH group by —Cl,

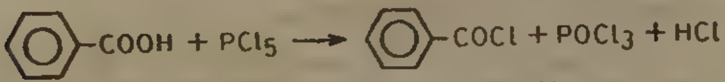
e.g., phosphorus pentachloride, phosphorus trichloride and thionyl chloride.



(where R=alkyl or alyl group)

For example :

$$CH_3COOH+SOCl_2 \longrightarrow CH_3COCl+SO_2+HCl$$



Benzoyl chloride

Thionyl chloride is preferred, because the by-products being gaseous, it is easy to purify the acid chloride formed.

Physical properties. Acid chlorides are colourless, hygroscopic liquids but their higher members are colourless solids with low melting points. They have pugent smell. The smell decreases with the increase of molecular masses. These are polar molecules. Hydrogen bonding is not possible in acid chlorides and consequently cannot associate as acids do. Thus, they have, as expected, lower boiling points than the corresponding acids. For example, the boiling point of acetic acid is 391 K while that of acetyl chloride is 324 K. Similarly the boiling point of benzoic acid is 523 K while benzoyl chloride boils at 470 K.

Chemical properties. Acyl chlorides are highly reactive compounds. The reactivity decreases with increase in size of the alkyl group. Many of their reactions involve the elimination of chlorine atom, usually as hydrogen chloride. Thus, when CH_3COCl is used, the CH_3CO group (the ethonyl group) is introduced into the other reacting molecule. Such reactions are termed ethanoylation (or acetylation or in general terms, acylation) reactions.

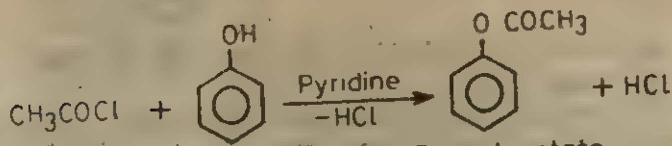
They react with water to give carboxylic acids, with alcohols and phenols to give esters, with ammonia and amines to give amides and with carboxylates to gives anhydrides.

1. Hydrolysis by water

$$CH_3COCl+HOH \xrightarrow{\text{Hydrolysis}} CH_3COOH+HCl$$

2. Ester formation (alcoholysis)

$$CH_3COCl + C_2H_5OH \xrightarrow[-HCl]{\text{Pyridine}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Reacts with pyridine}}{HCl}$$

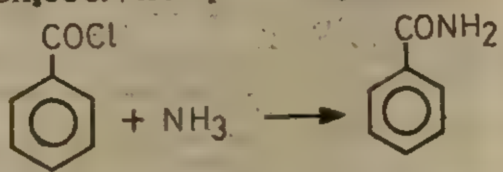


Phenylacetate

3. Amide formation (ammonolysis)

$$CH_3COCl + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2}$$

$$CH_3COCl + R'NH_2 \longrightarrow CH_3CONHR'$$



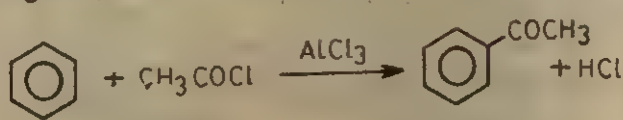
Benzamide

4. Anhydride formation

$$CH_3COCl + CH_3COOH \xrightarrow{\text{Pyridine}} \underset{\text{Acetic anhydride}}{CH_3CO.O.OCCH_3} + HCl$$

$$CH_3COCl + R'COONa \xrightarrow[\text{Distil}]{\text{Pyridine}} \underset{\text{Anhydride}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O-\overset{\displaystyle O}{\overset{\|}{C}}-R'}$$

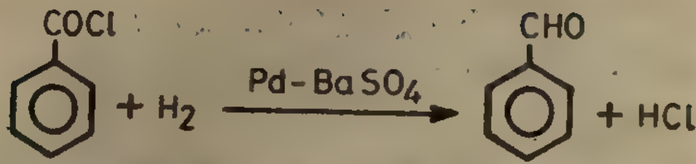
5. Friedel Crafts acylation. Acyl chlorides react with aromatic compounds in the presence of Lewis acids (*e.g.*, anhydrous $AlCl_3$) to give ketones.



Acetophenone

6. Rosenmund reaction. Acyl chloride is reduced by hydrogen in the presence of a partially poisoned palladium catalyst (reactivated by $BaSO_4$) to give aldehyde.

$$CH_3COCl + H_2 \xrightarrow{\text{Pd-BaSO}_4} CH_3CHO + HCl$$



Reactions of acid chloride are summarized in Fig. 8·9.

8·5.2. Acid Anhydrides

These are produced by the elimination of a molecule of water from two molecules of acid. The general formula is RCO.OCOR. Ethanoic anhydride (where R represents a methyl group) is the simplest member of the series.

Names of acid anhydrides are assigned by replacing the word 'acid' in the names of the carboxylic acids to anhydride. For example,

Acid Anhydride	$\begin{matrix} CH_3-CO \\ CH_3-CO \end{matrix}\Big> O$	$\begin{matrix} CH_3-CO \\ CH_3CH_2CO \end{matrix}\Big> O$	$\begin{matrix} C_6H_5CO \\ C_6H_5CO \end{matrix}\Big> O$
Common name	Acetic anhydride	Acetic propionic anhydride	Benzoic anhydride
IUPAC name	Ethanoic anhydride	Ethanoic propanoic anhydride.	Benzoic anhydride

Preparation. These are formed by the loss of a water molecule from two molecules of a carboxylic acid as follows :

(*i*) Dehydration of an acid by heating with phosphorus pentoxide :

$$2CH_3COOH \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

Dicarboxylic acids like succinic acid and phthalic acid can be easily dehydrated to the cyclic anhydrides by directly heating them in a procelain dish covered with a funnel with its stem closed. A deposit of the anhydride in the funnel is obtained.

(*ii*) Mixed anhydrides can be prepared by the reaction of an acid chloride with the sodium salt of another acid.

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + C_2H_5-\overset{\overset{O}{\|}}{C}-ONa \longrightarrow \begin{matrix} CH_3-\overset{\overset{O}{\|}}{C} \\ C_2H_5-\underset{\underset{O}{\|}}{C} \end{matrix}\Big> O + NaCl$$

Physical properties. Acid anhydrides of lower aliphatic acids are colourless liquids. Anhydrides of higher aliphatic acids and aromatic acids are colourless solids. Aliphatic acid anhydrides have unpleasant odour. The smell decreases with the increase of molecular mass.

Anhydrides are polar molecules but there is no possibility of hydrogen bonding. Their boiling points are higher than that of corresponding acids. For example, the bp of acetic anhydride is 413K while that of acetic acid is 391K. The reason for the higher boiling point of anhydrides is the larger size of the molecule (almost double mass) and hence the stronger van der Waals forces of attraction between them.

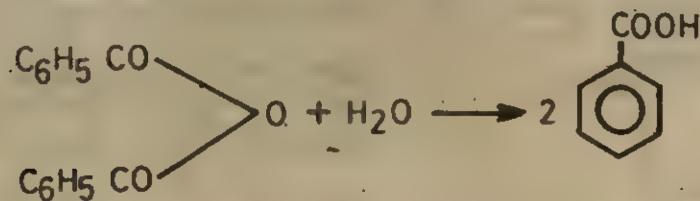
Acid anhydrides are soluble in organic solvents but almost insoluble in water.

Chemical properties. Acid anhydrides are less reactive than acid chlorides. All acylation reactions given by acid chlorides are given by them.

1. **Hydrolysis by water.** In view of their limited miscibility, hydrolysis is sometimes a delayed action, although once started, it can be vigorous.

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$$

Dilute aqueous alkali hydrolyses acid anhydride effectively to the corresponding acid.



2. **Alcoholysis.** Acid anhydride acetylates alcohols forming esters.

$$(CH_3CO)_2O + R\,OH \longrightarrow CH_3CO\,.\,OR + CH_3COOH$$

3. **Ammonolysis.** Ethanoic anhydride and other anhydrides react with ammonia to form amides.

$$(CH_3CO)_2O + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Ammonium acetate}}{CH_3CO\,.\,ONH_4}$$

$$(R\,CO)_2\,O + R'NH_2 \longrightarrow R\,CO\,NHR' + R\,COOH$$

4. **Reduction.** Ethanoic anhydride is reduced by $LiAlH_4$ to give ethanol.

$$(CH_3CO)_2\,O + 6[H] \xrightarrow{LiAlH_4} 2CH_3CH_2OH$$

5. **Friedel Crafts acylation.** Acid anhydride on reacting with aromatic hydrocarbon in the presence of Lewis acid yields ketones.

$$C_6H_6 + (CH_3CO)_2\,O \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + CH_3COOH$$

Acetic anhydride may be distinguished from acetyl chloride as the products of hydrolysis do not form a precipitate on the addition of $AgNO_3$ and dilute HNO_3. Reactions of acid anhydrides are summarized in Fig. 8.9.

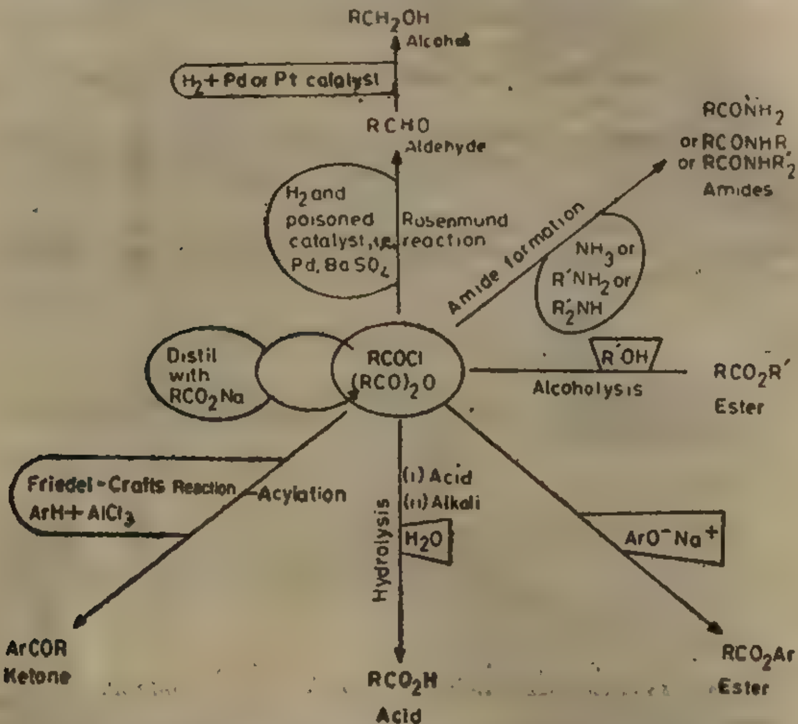


Fig. 8.9. Reactions of acid chlorides and anhydrides

8.5 2. Acid Amides

Amides may be thought of as derivatives of primary or secondary amines and carboxylic acids. Amides contain the

$$-\overset{\displaystyle O}{\overset{\|}{C}}-N<$$

grouping of atoms. An amide may be referred as aliphatic amide or an aromatic amide depending upon the nature of group attached to the $CO-NH_2$ group. The general formula of the amides is

$$R-C\begin{smallmatrix}\nearrow O \\ \searrow NH_2\end{smallmatrix}$$

the hydroxyl group of the acid being replaced by the $-NH_2$. R represents hydrogen or an alkyl radical. Amides are obtained from carboxylic acids and ammonia and its derivatives. With ammonia a primary amide, $RCONH_2$ is obtained. With a primary amine,

a secondary amide, R CO NHR′ and with a secondary amine a tertiary amide, $R\ CO\ N\begin{smallmatrix} R' \\ R' \end{smallmatrix}$ are obtained. Acid amides are assigned by changing the ending, *i.e.* acid of the name of corresponding carboxylic acid to amide. Thus the common name of $CH_3\ CO\ NH_2$ is acetamide. According to IUPAC system the amides also assume the word 'amide' at their end.

Acid amide	*Common name*	*IUPAC name*
$H-CO-NH_2$	Formamide	Methanamide
$CH_3\ CO\ NH_2$	Acetamide	Ethanamide
$C_6H_5\ CO\ NH_2$	Benzamide	Benzamide
$C_6H_5\ CO\ NH\ CH_3$	N-Methylbenzamide	N-Methylbenzamide

Preparation

(*i*) Carboxylic acids react with ammonia to yield ammonium salts, which on heating yield amides :

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow[\text{Catalyst}]{\text{Heat}} CH_3CONH_2 + H_2O$$

This method though used industrially is not convenient for laboratory preparation.

(*ii*) Amides are generally prepared by the reaction of ammonia (ammonolysis) or amines with acid chlorides or acid anhydrides.

$$R\ COCl \xrightarrow{NH_3} R\ CONH_2$$

$$(R\ CO)_2\ O \xrightarrow{2NH_3} R\ COONH_4 + R\ CONH_2$$

$$R\ COONH_4 \xrightarrow{\text{Heat}} R\ CONH_2 + H_2O$$

For example :

$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + NH_4Cl$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + \underset{\text{Ammonium acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONH_4}$$

$$\underset{\text{Acyl halide}}{R\ COCl} + \underset{\text{Primary amine}}{2R'\ NH_2} \longrightarrow \underset{\text{N-Alkyl acyl amide}}{R-CONHR'} + \underset{\text{Alkyl ammonium chloride}}{R'NH_3^+Cl^-}$$

For example :

$$\underset{\text{Chloride}}{CH_3-\overset{\overset{\large O}{\|}}{C}-Cl}+\underset{\text{Methyl amine}}{2CH_3NH_2}\longrightarrow\underset{\text{N-Methyl acetamide}}{CH_3-\overset{\overset{\large O}{\|}}{C}-NHCH_3}+\underset{\text{Methyl ammonium chloride}}{CH_3NH_3^+Cl^-}$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O}+\underset{\text{Dimethylamine (a Secondary amine)}}{2(CH_3)_2NH}\longrightarrow\underset{\text{N, N-Dimethyl acetamide}}{CH_3-\overset{\overset{\large O}{\|}}{C}-N\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}}+\underset{\text{Dimethyl ammonium acetate}}{CH_3-\overset{\overset{\large O}{\|}}{C}-O^-H_2N^+(CH_3)_2}$$

Physical properties.

Acid amides are colourless crystalline solids (except formamide which is a liquid). Lower aliphatic amides have a strong smell. Higher aliphatic and aromatic amides do not have any smell. Amides are polar compounds. Their melting points are much higher than those of their parent acids. Their boiling points are also higher compared to those of the corresponding acids or other derivatives (Table 8·4).

TABLE 8.4. Melting and boiling points of some acids and their functional derivative.

Compound	*Melting point*, K	*Boiling point*, K
Acetic acid	289·5	391
Acetyl chloride	161	324
Acetic anhydride	200	413
Acetamide	355	494
Benzoic acid	395	522
Benzoyl chloride	272	470
Benzoic anhydride	315	633
Benzamide	403	563

Intermolecular hydrogen bonding appears to be the reason of higher boiling points.

$$H-\overset{\overset{\large H}{|}}{N}-\overset{\overset{\large R}{|}}{C}=O\cdots H-\overset{\overset{\large H}{|}}{N}-\overset{\overset{\large R}{|}}{C}=O\cdots H-\overset{\overset{\large H}{|}}{N}-\overset{\overset{\large R}{|}}{C}=O\cdots$$

Hydrogen bonding in acid amides

Amides with low molecular masses are usually soluble in water. They are more soluble is water than the other derivatives due to hydrogen bonding with water.

Chemical properties

Unlike amides (RNH_2), amides are not basic in nature. The

$$\begin{array}{c} O \\ \| \\ R-C-\ddot{N}H_2 \end{array} \leftrightarrow \begin{array}{c} \bar{O} \\ | \\ R-C-\ddot{N}H_2 \\ + \end{array} \leftrightarrow \begin{array}{c} \bar{O} \\ | \quad + \\ R-C=NH_2 \\ + \end{array}$$

absence of a lone pair of electrons on nitrogen explains the neutral character of amides (suggested through resonating structures). They are less reactive towards nucleophilic reagents (unlike acid halides). Hence, they cannot be used as acylating reagents.

(*i*) **Hydrolysis.** Amides are hydrolyzed on boiling with either acid or alkali. They are less susceptible to hydrolysis than acid anhydrides or acid chlorides.

$$RCONH_2+NaOH \longrightarrow RCOONa+NH_3$$
$$RCONH_2+HCl+H_2O \longrightarrow RCOOH+NH_4Cl$$

(*ii*) **Dehydration.** Amides, an heating, are dehydrated by phosphorus pentoxide to form nitriles (also known as cyanides).

$$RCONH_2 \xrightarrow[\text{Heat}]{P_2O_5} R-C\equiv N+H_2O$$

(*iii*) On treating with ice-cold nitrous acid, primary amides give carboxylic acids and nitrogen.

$$RCONH_2+HONO \rightarrow \begin{array}{c} R-C-OH \\ \| \\ O \end{array} +N_2+H_2O$$

The evolution of nitrogen with nitrous acid is a characteristic of the $-NH_2$ group. This reaction serves as a method for a quantitative determination of amides.

(*iv*) Amides are reduced by heating with sodium in alcohol or with $LiAlH_4$ or by hydrogen under pressure.

$$RCONH_2+2H_2 \longrightarrow RCH_2NH_2+H_2O$$

(*v*) Amide reacts with bromine water and warm alkali to form a primary amine, containing one carbon atom less than the number of carbon atoms in the amide. This reaction takes place in two stages.

$$CH_3CONH_2+Br_2 \longrightarrow HBr+\underset{\text{Bromoethanamide}}{CH_3CONHBr}$$

$$CH_3CONH\,Br+3NaOH \longrightarrow NaBr+Na_2CO_3+H_2O+CH_3NH_2$$

The reaction involves molecular rearrangement in which the alkyl group migrates over to nitrogen atom. This reaction is known as **Hoffmann's degradation reaction.** This reaction is useful to prepare a lower homologue from a higher one.

The reactions of amides and their methods of preparation are given in Fig 8.10.

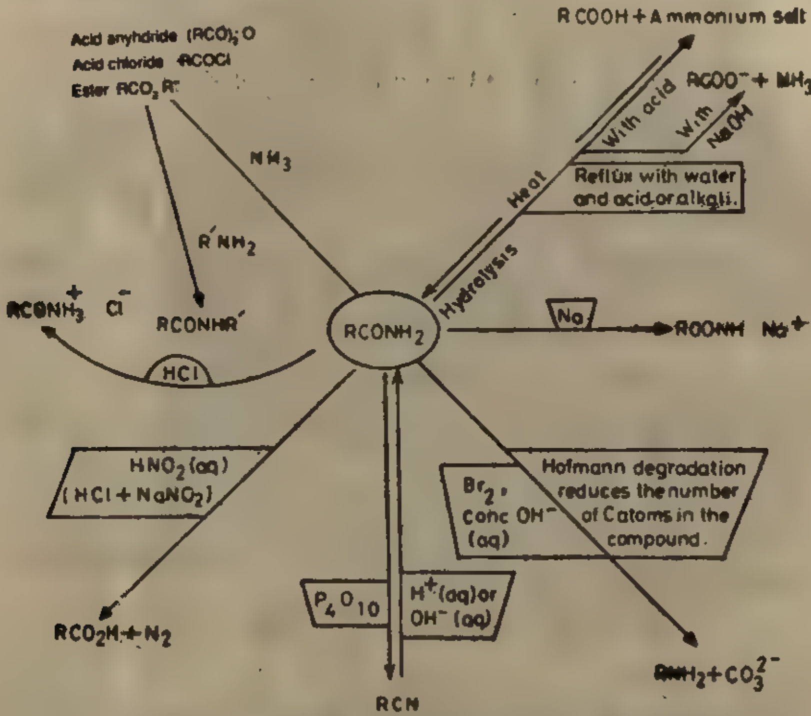


Fig. 8.10. Reactions of amides

Acetanilide, the amide of acetic acid and aniline, which is sometimes called **antifebrin**, is used to treat headaches, neuralgia, and mild fevers. The polymeric amides, also called polyamides are important class of compounds. Nylon 66 (Unit-15) is the best known polymeric amide.

8.5.3. Esters

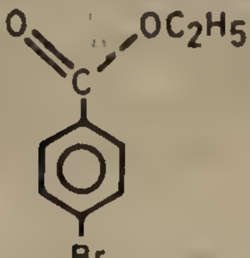
Esters are fragrant organic compounds produced by the reaction of an organic acid with an alcohol. Their general formula is $R-\overset{\overset{O}{\|}}{C}-OR'$, where R and R' may be the same or different alkyl groups. The functional group of esters which determines their characteristic behaviour may be written as :

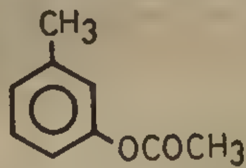
$$-\overset{\overset{O}{\|}}{C}-OR' \quad \text{or} \quad -CO-OR' \quad \text{or} \quad -COOR' \; (R' = \text{from alcohol})$$

They are superficially analogous to salts of the carboxylic acids. Unlike salts, they are non-ionic and more typically organic.

Esters are nearly always called by their common (trivial) names. They are named by changing the '—ic' ending of the acid from which they derive to '-ate' preceded by the alkyl radical of the parent alcohol. For example, an ester prepared from acetic acid and methyl alcohol is called methyl acetate. The trival and IUPAC names of a few simple esters are given below :

Formula	*Alcohol*	*Trivial name*	*IUPAC name*
$CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$	CH_3OH	Methyl acetate	Methyl ethanoate
$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$	C_2H_5OH	Ethyl acetate	Ethyl ethanoate
$CH_3CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$	C_2H_5OH	Ethyl propionate	Ethyl propanoate
$CH_3(CH_2)_2-\overset{\overset{O}{\|}}{C}-OC_3H_7$	C_3H_7OH	Propyl butyrate	Propyl butanoate





3-Methyl phenyl acetate

Ethyl-4-bromobenzoate

Isomerism. Esters show chain isomerism of the hydrocarbon groups. A compound with molecular formula, $C_4H_8O_2$ represents two isomeric esters and one acid.

$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} \qquad \underset{\text{Methyl propanoate}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-OCH_3} \qquad \underset{\text{Butanoic acid}}{CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}-OH}$$

The two esters differ in respect of the carbon atoms about the ester group and are called metamers (metamerism).

Preparation of Esters

(*i*) **From an acid and alcohol.** Esters are produced by the reaction of a carboxylic acid and an alcohol in an acid (conc. H_2SO_4) catalyzed equilibrium reaction :

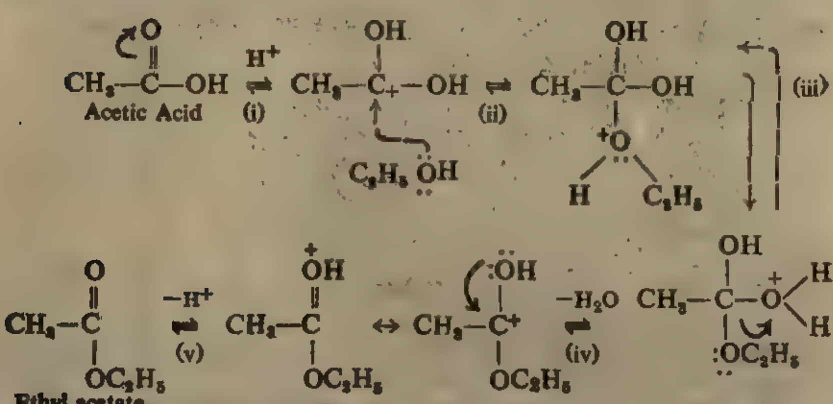
$$\underset{\|}{\overset{O}{}}\!\!\!\!R-C-\boxed{OH + H}OR' \underset{\text{Hydrolysis, H}^+}{\overset{\text{Esterification, H}^+}{\rightleftharpoons}} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

In order to get a good yield of ester, the equilibrium must be displaced to the right. According to the Le Chatelier's principle, the removel of water will effectively force the reaction in the direction of esterification. Or, use of alcohol in a large excess will also favour the process of esterification.

The **mechanism of esterification** involves :

(*i*) Protonation of the carbonyl oxygen, resulting in increased polarization of the $>C=O$ group, (*ii*) The carbonyl carbon is then attacked by alcohol molecule, (*iii*) The transfer of proton to one of the —OH group takes place, (*iv*) The —OH group leaves as water molecules giving protonated ester, and (*v*) The protonated ester loses a proton.

The mechanism of removal of water by condensation is shown below :



With an excess of water in the presence of a trace of acid, hydrolysis of the ester takes place and the free alcohol and carboxylic acid are obtained. This method is also used for the production of esters.

(*ii*) **From an acid anhydride or an acid chloride and alcohol (alcoholysis).** An acid chloride or anhydride when reacts with alcohol, an ester is obtained.

$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} + C_2H_5OH \xrightarrow[-HCl]{\text{Pyridine}} \underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5}$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5-\overset{\overset{\large O}{\|}}{C}-Cl}+CH_3OH \xrightarrow[-HCl]{NaOH} \underset{\text{Methyl benzoate}}{C_6H_5-\overset{\overset{\large C}{\|}}{C}-OCH_3}$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O}+C_2H_5OH \xrightarrow[-HCl]{\text{Pyridine}} \underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{\large O}{\|}}{C}-OC_2H_5}+\underset{\text{Acetic acid}}{CH_3COOH}$$

(*iii*) **From silver salt of an acid and haloalkanes.** A silver salt of a carboxylic acid on beating with ethanolic solution of alkyl halide gives ester.

$$\underset{\text{Silver salt}}{RCOOAg}+\underset{\text{Alkyl iodide}}{R'I} \longrightarrow \underset{\text{Ester}}{RCOOR'}+AgI$$

For example :

$$\underset{\text{Silver acetate}}{CH_3COOAg}+\underset{\text{Ethyl iodide}}{C_2H_5I} \longrightarrow \underset{\text{Ethyl acetate}}{CHCOOC_2H_5}+AgI$$

Physical properties

Esters are non-toxic, non-corrosive and colourless liquids with pleasant and fruitly odours. The lower members are volatile liquids (lighter than water). The higher esters are wax-like solids. Esters usually have lower boiling points than acids or alcohols of comparable molecular mass. The lower esters are fairly soluble in water. Their solubility decreases with increase in molecular mass. They are soluble in organic solvents, *e.g.*, benzene, ether, alcohol, *etc.*

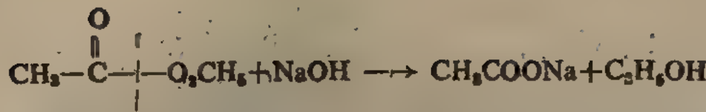
Chemical properties

Esters are less reactive than other acid derivatives. Esters undergo the nucleophilic displacement reactions, *viz.*, displacement of OR′ group by —OH or —NH_2 and so on.

(*i*) **Hydrolysis.** They are hydrolyzed on refluxing with acids or dilute alkalis. Both acid and alkali work as catalyst. It involves the cleavage of the bond between the oxygen and acyl group, *i.e.* $R-\overset{\overset{O}{\|}}{C}-|-OR'$. Esters on treatment with mineral acid (H_2SO_4 or HCl) yield alcohol and acid.

$$CH_3-\overset{\overset{\large O}{\|}}{C}-|-OC_2H_5+HOH \xrightarrow[\text{Catalyzed}]{\text{Acid}[H^+]} CH_3COOH+C_2H_5OH$$

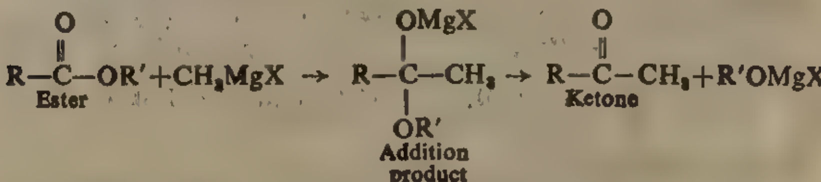
Thus hydrolysis is the reverse of esterification. Treatment of esters with alkali results in hydrolysis to form the sodium salts of the freed carboxylic acids.

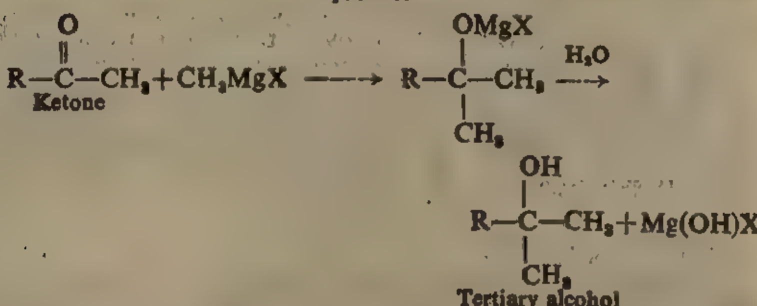


This reaction is also known as **saponification** as the hydrolysis of natural oils and fats (esters of glycerol) by alkali results in the formation of soap.

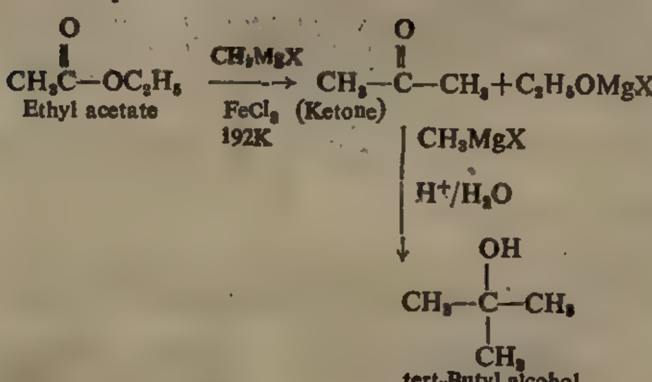
$$\underset{\text{Fat}}{C_3H_5(O_2CC_{17}H_{35})_3} + 3NaOH \longrightarrow \underset{\text{Glycerol}}{C_3H_5(OH)_3} + \underset{\text{Soap}}{3C_{17}H_{35}-COO^-Na^+}$$

(*ii*) **Reaction with organo magnesium halide (Grignard reagent).** Esters give tertiary alcohols with Grignard reagent. By carefully regulating the conditions it is possible to isolate the ketone intermediate. Under normal conditions this ketone will react further to give tertiary alcohol.





For example :



(*iii*) Esters form amides with ammonia

$$RCOOR'+NH_3 \rightarrow RCONH_2+R'OH$$

(*iv*) Esters are reduced to alcohols by refluxing with sodium in alcohol (or by high pressure hydrogenation in the presence of a catalyst.

$$CH_3COOC_2H_5+4[H] \rightarrow 2CH_3CH_2OH$$

(*v*) When an ester is treated with an alcohol in the presence of an acid (H_2SO_4 or HCl), a new ester with the alkyl group of the new alcohol part is obtained.

$$RCOOR'+R''-OH \xrightarrow{H^+} RCOOR''+R'-OH$$

The reaction is known as **transestrification.**

Reactions of esters are summarized in Fig 8.11.

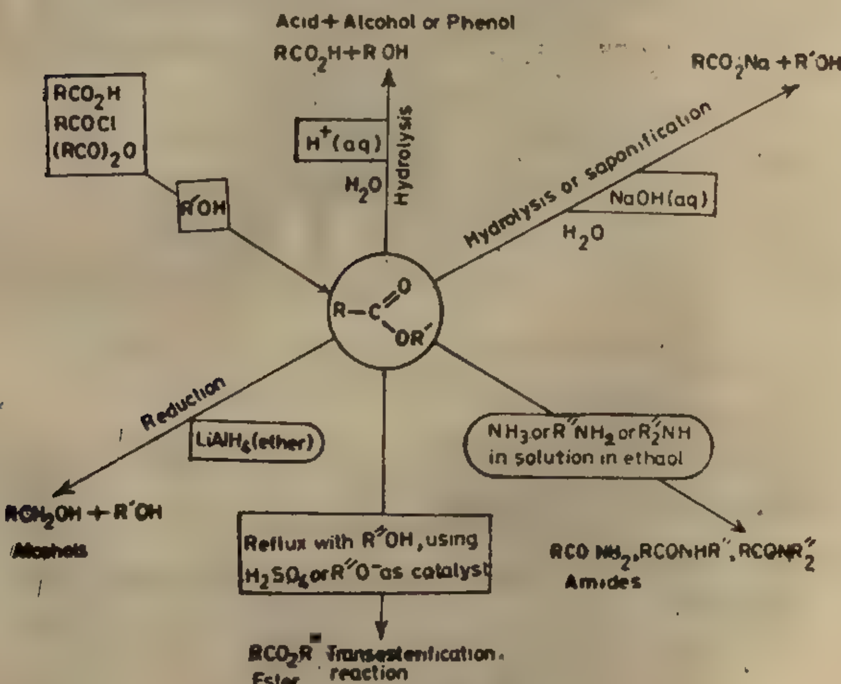


Fig. 8.11. Reactions of esters

Relationship between carboxylic acids and other compounds is shown through Fig. 8.12.

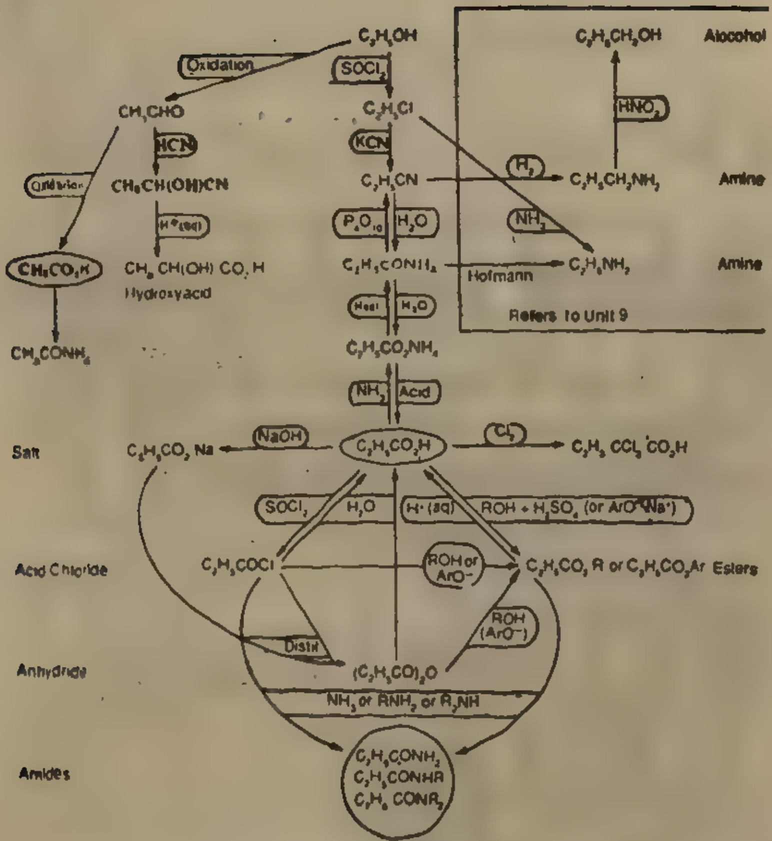


Fig. 8.12 Relationships between carboxylic acids and other compounds

Uses of Esters

Esters are used for making synthetic flavours and essences. They are also used as perfumes, solvents and plasticizers. Higher esters are used for making soaps.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

8·1. Choose the correct answer of the four alternatives given for the following questions :

(*i*) Base catalyzed aldol condensation occurs with (*I.I.T. 1984*)

(*a*) propionaldehyde (*b*) benzaldehyde

(*c*) 2-methylpropionaldehyde

(*d*) 2, 2-dimethylpropionaldehyde.

(*ii*) Which of the following compounds will give a yellow precipitate with iodine and alkali ? (*I.I.T. 1984*)

(*a*) 2-hydroxypropane, (*b*) acetophenone

(*c*) methyl acetate (*d*) acetamide.

(*iii*) Which of the following compounds will react with ethanolic KCN ? (*I.I.T. 1984*)

(*a*) ethyl chloride (*b*) acetyl chloride
(*c*) chlorobenzene (*d*) benzaldehyde.

(*iv*) Which of the following compounds is oxidized to prepare methyl ethyl ketone ? (*I.I.T. 1987*)

(*a*) 2-propanol (*b*) 1-butanol
(*c*) 2-butanol (*d*) tert-butyl alcohol.

(*v*) An organic compound does not give Lucas test but gives a positive test with phenylhydrazine. On standing in air, this compound is converted to a neutralization equivalent of 74. The compound is

(*a*) CH_3CH_2CHO (*b*) $CH_3CH_2CH_2OH$
(*c*) CH_3COCH_3 (*d*) $CH_3CH(OH)CH_3$

(*vi*) Which of the following reagents is not used in making derivatives of carbonyl compounds ?

(*a*) 2, 4-dinitrophenyl hydrazine (*b*) phenylhydrazine
(*c*) 2, 4-dinitrobenzene (*d*) hydroxylamine hydrochloride.

(*vii*) A mixed aliphatic anhydride is usually prepared by

(*a*) treating a salt of a carboxylic with an aryl chloride
(*b*) Cannizzaro reaction
(*c*) treating an alcohol with an aryl chloride
(*d*) by heating a mixture of two different carboxylic acids with phosphorus pentoxide.

(*viii*) Ethene reacts with cold dilute $KMnO_4$ to yield

(*a*) CH_3CHO (*b*) $CH_2(OH)CH_2(OH)$
(*c*) HCHO (*d*) CH_3OH

(*ix*) Which of the following does not give Cannizzaro reaction ?

(*a*) methanal (*b*) benzaldehyde
(*c*) ethanal (*d*) 2, 2-dimethyl propanal.

(*x*) Fehling's reagent is used in the detection of

(*a*) —COOH group (*c*) —OH (phenolic group)
(*b*) $-\underset{\displaystyle H}{\underset{|}{C}}=O$ group (*d*) $>C=O$.

(*xi*) A mixed salt of calcium acetate formate on dry distillation, gives

(*a*) formaldehyde (*b*) acetic acid
(*c*) acetone (*d*) acetaldehyde

(*xii*) Propionic acid when reacted with bromine in the presence of phosphorus forms

(*a*) $CH_3CHBrCOOH$ (*b*) CH_2BrCH_2COOH
(*c*) $CH_3C(Br)_2COOH$ (*d*) CBr_3CH_2COOH

(*xiii*) Which of the following compounds cannot undergo an aldol condensation ?

(*a*) C_6H_5CHO (*b*) $CH_3CH_2COCH_3$
(*c*) CH_3CHO (*d*) $C_6H_5CH_2CHO$

(*xiv*) Acetamide and ethyl acetate can be distinguished by reacting with
(*a*) bromine water (*b*) alkaline $KMnO_4$
(*c*) aqueous HCl and heat (*d*) aqueous NaOH and heat.

8.2. State if the following statements are True (T) or False (F)

(*i*) Ethers are more volatile than alcohols.
(*ii*) Formaldehyde and other aldehydes reduce Cu (II) to Cu(s).
(*iii*) Aldehydes with no H atom on the carbon atom next to the carbonyl group give Cannizzaro reaction.
(*iv*) The boiling point of ethanoic acid is lower than that if either ethanol which has the same number of carbon atoms or propan-1-ol which has the same relative molecular mass.
(*v*) Chloroacetic acid is a stronger acid than acetic acid.
(*vi*) Benzoic acid is highly soluble in water.
(*vii*) Esters are converted to alcohols by the use of high pressure hydrogen and a catalyst.
(*viii*) The hydrolysis of an ester by alkali is sometimes called saponification.
(*ix*) Acid anhydrides have the general formula $(RCO)_2O$.
(*x*) Nitrous acid reacts with primary amides to give carboxylic acids and ammonia.

8.3. Fill in the blanks with suitable words :

(*a*) The carboxylic acids display.........acidic properties.
(*b*) ....are formed by the reaction between a carboxylic acid and an alcohol.
(*c*) The general formula for esters is.........
(*d*) Nitroglycerine is an.........ester.
(*e*) An aldehyde can be detected by its easy.........to a.........
(*f*) In Tollen's reagent the oxidizing substance is.........which is reduced to.........
(*g*) Paraformaldehyde is a.........of formaldehyde.
(*h*) ....are prepared by the oxidation of secondary alcohols.
(*i*) Ketones are.........to oxidize further.
(*j*) ....may be prepared by the oxidation of isopropyl alcohol.
(*k*) Alcohol can be produced by the process of.........
(*l*) Phenol is also called.........since phenols exhibit acid properties.
(*m*) Carboxylic acids may be prepared by the...........of corresponding aldehydes.

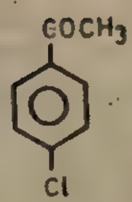
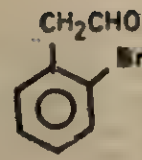
SHORT ANSWER QUESTIONS

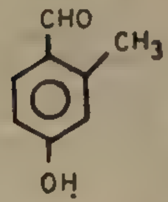
8.4. Give IUPAC names of the following compounds :

(*i*) $CH_3-CH_2-O-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(*ii*) $CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CHO$

(*iii*) $CH_3-CO\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2-CH_2Cl$

(iv)  (v) 

(vi) 

(ix) 

(vii) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CONH_2$ (viii) $(C_6H_5CO)_2O$

8.5. (*a*) Comment on the following :

(*i*) The boiling points of ethers are lower than their isomeric alcohols.

(*ii*) The boiling points of aldehydes and ketones are lower than the corresponding alcohols and acids.

(*iii*) The boiling points of acids are higher than the corresponding alcohols.

(*b*) Arrange the following in increasing order of boiling points :

(*i*) $C_2H_5-O-C_2H_5$, C_4H_9COOH, C_6H_9OH,

(*ii*) C_3H_7-CHO, $CH_3-CO-C_2H_5$, $C_2H_5COOCH_3$, $(CH_3CO)_2O$

8.6. Give reasons for the following :

(*i*) Chloroacetic acid is stronger than acetic acid.

(*ii*) The order of reactivity of halogen acids with ethers is HI > HBr > HCl.

(*iii*) In the preparation of an ester by the reaction of a carboxylic acid and an alcohol, the ester is distilled as fast as it is formed.

(*iv*) During the preparation of ammonia derivatives from aldehydes or ketones, pH of the reaction is carefully controlled.

(*v*) Phenyl methyl ether reacts with HI to give phenol and methyl iodide and not iodo benzene and methyl alcohol.

8.7. Write the names and structures of the products formed in the following reactions :

(*i*) Reaction of acetyl chloride with H_2 gas in the presence of palladium as catalyst.

(*ii*) Oxidation of toluene with chromic oxide in acetic anhydride.

(*iii*) Friedel-Crafts reaction between acetyl chloride and toluene in presence of $AlCl_3$.

(*iv*) Dehydrogenation of propanol over heated copper.

(*v*) Addition of HCN to acetone.

(*vi*) Addition of $NaHSO_3$ to acetaldehyde.

(*vii*) Reaction of seimcarbazide ($NH_2CONHNH_2$) with formaldehyde.

(*viii*) Reaction of ethyl magnesium bromide with 2-butanone.

(*ix*) Reaction of thionyl chloride with benzoic acid.

(*x*) Oxidation of ethyl benzene with alkaline $KMnO_4$.

8·8. How will you convert

(*i*) propanoic acid to acetic acid

(*ii*) acetophenone to ethyl benzene

(*iii*) acetophenone to benzoic acid

(*iv*) anisole to *ortho*-nitroanisole

(*v*) acetamide to ethyl amine

(*vi*) benzoic acid to 3-nitrobenzoic acid

(*vii*) propanoic acid to propanol

(*viii*) acetaldehyde to isopropyl alcohol

(*ix*) acetone to tert-butyl alcohol ?

TERMINAL QUESTIONS

8.1. What are ethers ? How do they differ from alcohols ? Distinguish between simple and mixed ethers.

8.2. Give two methods for preparing ethers and give two specific examples for each method.

8.3. What is Williamson synthesis of ethers ? Give the synthesis of diethyl ether by this method.

8.4. What happens when ether undergoes cleavage ?

8.5. How does ether show its basic properties ? Illustrate.

8.6. What are aldehydes and ketones ? What are the general methods of obtaining aldehydes ?

8.7. Discuss the oxidation and reduction reactions of aldehydes and ketones.

8.8. Write notes on the following :

(*i*) Structure of carbonyl group (*ii*) Rosenmund reaction

(*iii*) Friedel-Crafts acylation (*iv*) Trioxane.

8.9. Discuss the reactions of aldehydes and ketones under the following heads :

(*i*) Addition reactions (*ii*) Oxidation

(*iii*) Reduction

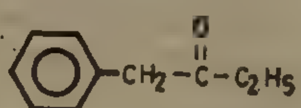
8.10. What is aldol condensation ? What happens when aldol is dehydrated ?

8.11. Give the common and IUPAC names for the following compounds :

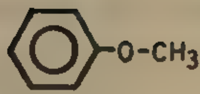
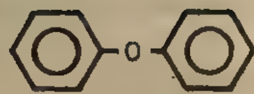
(*i*) $CH_3CH_2CH_2CHO$

(*ii*) $CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}H-CHO$

(*iii*) $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_3$



(iv)

$C_2H_5OC_2H_5$  

(v) (vi) (vii)

8.12. What are carboxylic acids ? Comment on their nomenclature.

8.13. What are functional derivatives of carboxylic acids ? Give three examples. Suggest a method of preparation for each of the three.

8.14. What are the various methods of preparing carboxylic acids ?

8.15. Comment on the acidity of carboxylic acids, Give at least four acidic properties in support of your answer.

8·16. Write notes on the following :

(i) Decarboxylation of carboxylic acid, and

(ii) Salt-formation of a carboxylic acid and reactions of some acid salts.

8.17. What are esters ? Give some of their characteristics.

8.18. (a) Discuss the mechanism of esterification.

(b) Describe the two reactions of ethyl acetate.

8·19. How are carboxylic acids and esters obtained from aldehydes and alcohols ?

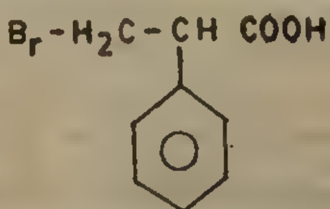
8·20. Discuss the reactions of esters involving the cleavage of bond between the oxygen and the acyl group.

8.21. Give the common and IUPAC names for the following compounds :

(i) CH_3CH_2COOH, (ii) C_6H_5COOH

(iii) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$ (iv) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

(v) $CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-OC_2H_5$ (v) $(CH_3CO)_2O$

(vii) 

8.22. What do you understand by the following terms :

(i) Saponification (ii) Esterification

(iii) Hydrolysis (iv) Nomenclature.

8.23. Mention one difference between the following pairs :

(a) carboxyl and carbonyl

(b) acid and acid anhydride

(c) aldehyde and ketone

(d) alcohol and phenol

(e) amine and amide

8.24. Identify the functional group in the compounds given below :

(a) $C_6H_5\overset{\overset{O}{\|}}{C}CH_3$ (b) CH_3CH_2COOH

(c) $CH_3CO_2C_2H_5$ (d) $(CH_3)_3COH$

(e) C_6H_5OH

8.25. Complete the following reactions :

(a) A secondary alcohol $\xrightarrow[H_2SO_4]{K_2Cr_2O_7}$?

(b) A tert-alcohol $\xrightarrow[H_2SO_4]{K_2Cr_2O_7}$?

(c) 1-Pentanal $\xrightarrow[H_2SO_4]{K_2Cr_2O_7}$?

(d) $(CH_3)_2CHOH$ $\xrightarrow[Heat]{Cu}$?

(e) $C_2H_5OC_2H_5 + HI$ $\xrightarrow{Cold}$?

8.26. (i) Why is there no such compound as ethanone ?

(ii) How would you expect C_6H_5CHO to compare with ethanal in its readiness to undergo nucleophilic addition ?

(iii) Name the compound to which ethanol might be oxidized.

(iv) Why is ethanal an important industrial chemical ?

(v) Why are carboxylic acids stronger acids than alcohols ?

8.27. (a) How are carboxylic acids obtained using :

(i) Primary alcohols (ii) Alkyl cyanides (iii) Aldehydes.

(b) How is acetic acid manufactured ?

8.28. Give one method for converting a carboxylic acid into an :

(i) Acid chloride (ii) Acid anhydrides

(iii) Acid amide.

8.29. (a) What is the HVZ reaction ?

(b) Give the method of synthesis of an α-amino acid and an α-hydroxy acid using the HVZ reaction.

8.30. Discuss the behaviour of acid chlorides, acid anhydrides and acid amides when subjected to hydrolysis.

8.31. Explain why ethoxyethane is

(a) More volatile than ethanol,

(b) Less dense than water, and

(c) A better solvent than water for organic compounds.

8.32. (a) Explain why there is intermolecular hydrogen bonding in $C_6H_5CH_2OH$ but not in C_6H_5CHO.

(b) State two reactions of aldehydes which are also characteristic of ketones and two which are not shared by ketones. What is the reason for the difference ?

8.33. How can the following conversions be brought about ?

(*i*) $CH_3COCH_3 \longrightarrow CH_3COCH_2OH$

(*ii*) $CH_3COCH_3 \longrightarrow CH_3CH{=}CH_2$

(*iii*) $C_6H_5CHO \longrightarrow C_6H_5CH_2Br$

(*iv*) $CH_3COOH \longrightarrow CH_3CONH_2$

(*v*) $CH_2{=}CH_2 \longrightarrow CH_3COOH$

(*vi*) $C_6H_5CH_3 \longrightarrow C_6H_5COOH$

8.34. What chemical tests would you use to distinguish between the following compounds ?

(*i*) C_6H_5CHO, CH_3COCH_3, C_6H_5COOH

(*ii*) $HCOOH$, CH_3COOH

(*iii*) C_6H_5CHO, $C_6H_5CH_2OH$, $C_6H_5COCH_3$

(*iv*) $CH_3COC_2H_5$, $CH_3COOC_2H_5$

8.35. To what extent does the carboxyl group $-\underset{\underset{O}{\|}}{C}-OH$ show properties typical of

(*a*) The group $-\underset{\underset{O}{\|}}{C}-$ group, (*b*) The OH group ? To what extent are its properties different from those of either of these groups ?

8.36. Predict the formulae of the products of the following reactions :

(*i*) $CH_3COOH + Ca(OH)_2\,(aq) \longrightarrow$

(*ii*) $CH_3CH_2COOH + PBr_3 \longrightarrow$

(*iii*) $(CH_3CO)_2O + C_6H_5NH_2 \longrightarrow$

(*iv*) $CH_3COC_2H_5 + H_2 \xrightarrow{Ni}$

(*v*) $C_6H_5CHO \xrightarrow{KMnO_4}$

(*vi*) $CH_3CH_2CHO + Cl_2 \longrightarrow$

ANSWERS TO SELF ASSESSMENT QUESTIONS

8.1. (*i*) (*a*) and (*c*) (*ii*) (*a*) (*iii*) (*a*) and (*d*) (*iv*) (*c*) (*v*) (*a*)
(*vi*) (*c*) (*vii*) (*a*) (*viii*) (*b*) (*ix*) (*c*) (*x*) (*c*)
(*xi*) (*d*) (*xii*) (*a*) (*xiii*) (*a*) (*xiv*) (*d*)

8.2. (*i*) T (*ii*) F (*iii*) F (*iv*) F (*v*) T
(*vi*) F (*vii*) T (*viii*) T (*ix*) T (*x*) F

8.3. (*a*) slight. (*b*) esters.
(*c*) RCOOR′. (*d*) explosive.
(*e*) oxidation, carboxylic acid, (*f*) Ag^+, Ag(s),
(*g*) polymer. (*h*) ketones.
(*i*) difficult. (*j*) acetone.
(*k*) fermentation. (*l*) carbolic acid.
(*m*) oxidation.

8.4. (*i*) 2-Methyl propyl ethyl ether.
(*ii*) 3-Methyl hexanal.
(*iii*) 5-Chloro 3-ethyl 2-pentanone.
(*iv*) p-Chloro phenyl methyl ketone.

(*v*) 2-(o-Bromophenyl) 1-ethanal.

(*vi*) 4-Hydroxy 2-methyl benzaldehyde.

(*vii*) 2-Methyl propanamide.

(*viii*) Benzoic anhydride.

(*ix*) Anisaldehyde (p-methoxy-benzaldehyde).

8.5. (*a*) (*i*) Ethers are isomeric with alcohols. Unlike alcohols, ethers do not experience any molecular association by intermolecular hydrogen bonding because of lack of polarity in ethers. Hence, ethers have lower boiling points than that of isomeric alcohols.

(*ii*) Aldehydes and ketones cannot form any intermolecular hydrogen bonds like alcohols as the hydrogen in these compounds is attached to carbon atoms only. Therefore, they have lower boiling points than the corresponding alcohols or carboxylic acids.

(*iii*) Both acids and alcohols are polar compounds. They form associated molecules through hydrogen bonding. Acids form dimers also, hence, their boiling points are higher than alcohols of comparable molecular masses.

(*b*) (*i*) $C_2H_5OC_2H_5 < C_4H_9OH < C_4H_9COOH$

(*ii*) $CH_3COC_2H_5 < C_3H_7CHO < C_2H_5COOCH_3 < (CH_3CO)_2O$

8.6. (*i*) Chlorine, an electron withdrawing group, withdraws electrons from the carboxyl group and thus facilitates the removal of H^+. As a result, chloroacetic acid is a stronger acid than acetic acid.

(*ii*) HI is the strongest acid. The proton released attacks the ether which in turn is attacked by the conjugate base *i.e.* I being easily polarisable as compared to Br^- and Cl^-.

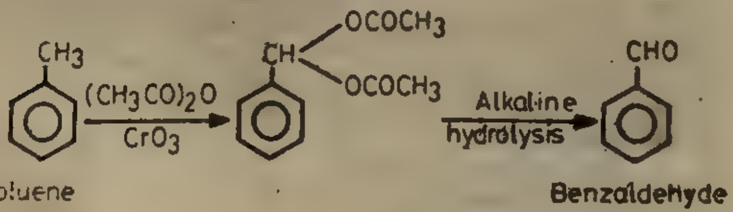
(*iii*) The reaction of a carboxylic acid and an alcohol is reversible. Therefore, the ester is distilled as fast as it is formed to prevent the reversible reaction.

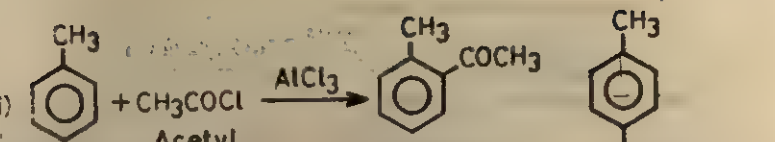
$$RCOOH + R'{-}OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

(*iv*) During the preparation of ammonia derivatives from carbonyl compounds, if pH of the reaction is not controlled, ammonia would react to form a salt such as $R{-}\overset{+}{N}H_3\overset{-}{X}$ which will not react with carbonyl compound to form derivatives.

(*v*) The C—O—C bond present in ether is broken as H^+ of HI attacks the ether and form an unstable product which in turn is attacked (nucleophilic attack) by I^- forming phenol and methyl iodide.

8.7. (*i*) $CH_3{-}\overset{O}{\overset{\|}{C}}{-}Cl + H_2 \xrightarrow{Pd} CH_3{-}CHO + HCl$
Acetaldehyde

(ii) 

(iii) 

Toluene + Acetyl chloride $\xrightarrow{AlCl_3}$ o-Tolyl methyl ketone + p-Tolyl methyl ketone

(iv) $CH_3-\underset{\substack{|\\OH}}{CH}-CH_3 \xrightarrow{Cu/573\,K} CH_3COCH_3$
2-Propanol — Acetone

(v) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O+HCN \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\CN\end{matrix}$
Acetone — Acetone cyanohydrin

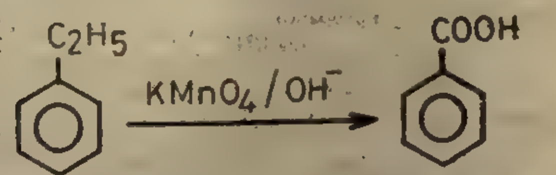
(vi) $CH_3CH=O+\overset{+}{Na}H\overset{-}{SO_3} \longrightarrow CH_3CH<\!\!\begin{matrix}OH\\ \overset{-}{S}O_3\overset{+}{Na}\end{matrix}$

(vii) $HCHO+H_2N.NHCONH_2 \longrightarrow HCH=N.NHCONH_2+H_2O$
Semicarbazide — Semicarbazone

(viii) $CH_3COCH_2CH_3+Mg<\!\!\begin{matrix}CH_3\\Br\end{matrix} \longrightarrow \begin{matrix}H_3C\\H_3CH_2C\end{matrix}\!\!>C<\!\!\begin{matrix}OMgBr\\CH_3\end{matrix}$
2-Butanone

$\xrightarrow{\text{Hydrolysis}} \begin{matrix}H_3C\\H_3CH_2C\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\CH_3\end{matrix}+Mg<\!\!\begin{matrix}OH\\Br\end{matrix}$
2-Methyl 2-butanol

(ix) $C_6H_5COOH+SOCl_2 \longrightarrow C_6H_5COCl+SO_2+HCl$
Benzoyl chloride

(x) 

Ethyl benzene $\xrightarrow{KMnO_4/OH^-}$ Benzoic acid

8.8. (i) **Propanoic acid to acetic acid**

$CH_3CH_2COOH \xrightarrow{NH_3} CH_3CH_2COONH_4 \xrightarrow{\text{Heat}} CH_3CH_2CONH_2$
Propanoic acid — Ammouium propanoate

$\xrightarrow[\text{Hoffmann reaction}]{Br_2+KOH} CH_3CH_2NH_2 \xrightarrow{HONO} CH_3CH_2OH$
Ethyl amine — Ethyl alcohol

$\xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$
Acetaldehyde — Acetic acid

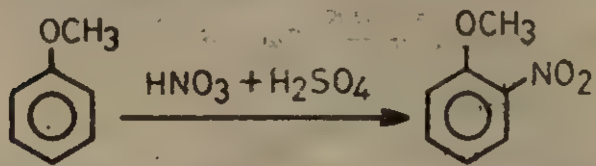
(*ii*) Acetophenone to ethyl benzene

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 4[H] \xrightarrow[HCl]{Zn/Hg} \underset{\text{Ethyl benzene}}{C_6H_5CH_2CH_3} + H_2O$$

(*iii*) Acetophenone to benzoic acid

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow{[O]} \underset{\text{Phenyl glyoxylic acid}}{C_6H_5COCOOH} \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(*iv*) Aniosole to ortho-nitroanisole.

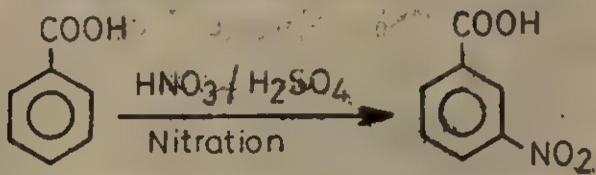


Anisole o-Nitroanisole

(*v*) Acetamide to ethylamine.

$$CH_3CONH_2 + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

(*vi*) Benzoic acid to 3-nitrobenzoic acid.



3-Nitrobenzoic acid

(*vii*) Propanoic acid to propanol.

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow{LiAlH_4} \underset{\text{Propanol}}{CH_3CH_2CH_2OH}$$

(*viii*) Acetaldehyde to isopropyl alcohol.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \quad \underset{\text{Methyl magnesium bromide}}{CH_3MgBr} \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHOMgBr \xrightarrow{HOH} \underset{\text{Isopropyl alcohol}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHOH}$$

(*ix*) Acetone to tert-butyl alcohol.

$$CH_3MgI + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}O \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\begin{matrix} OMgI \\ CH_3 \end{matrix} \xrightarrow{H_2O/H^+}$$

$$\underset{\text{tert-Butyl alcohol}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\begin{matrix} OH \\ CH_3 \end{matrix}} + Mg(OH)_2$$

□ □

UNIT 9

Organic Chemistry Based on Functional Group III

(Cyanides, Isocyanides, Nitrocompounds and Amines)

As a science, organic chemistry is less than 200 years old. Most historians of science date its origin to the early part of the nineteenth century, a time in which an erroneous belief was dispelled.

UNIT PREVIEW

9.1 Introduction.

9.2 Cyanides and isocyanides: nomenclature, preparation, physical properties, chemical properties, reactions, and uses.

9.3 Nitrocompounds : nomenclature, preparation, physical properties, chemical properties and reactions and uses.

9.4 Amines : nomenclature, isomerism, physical properties, chemical properties and reactions, analysis of amines, Distinction among three classes of amines and uses.

Self-assessment questions.

Terminal questions.

Answers to self assessment questions.

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Describe and give examples of the group of organic compounds called, cyanides, isocyanides, nitro and amines.
2. Deduce the IUPAC names of the organic compounds given the structural formula and vice versa.
3. Recognise and name the various compounds covered in this unit from the formulae.
4. Give the methods of preparation of the compounds included in this unit.
5. Correlate the variation observed in physical properties of these compounds with their structures.
6. Correlate the chemical reactions of compounds with their structures.
7. Emphasize the importance of diazonium salts.
8. Understand the terms : nucleophilic and electrophilic substitution.
9. Distinguish between different classes of amines.
10. List important uses of the compounds spanning the unit.

9.1. INTRODUCTION

The substitution of elements or radicals for one or more of the hydrogen atoms in a hydrocarbon results in the formation of many types of compounds, which are referred to as derivatives of the hydrocarbons. Derivatives of the hydrocarbons may be classified into groups or types of compounds depending on the atom or group of atoms substituted for the hydrogen atom. These groups are commonly called functional groups and determine the properties of the compound. Compounds with the same functional group exhibit very similar chemical properties. Compounds that make up each family of organic compounds are different from compounds of other families. In this unit, we shall be mainly concerned with the compounds that contain nitrogen.

The important functional groups in which nitrogen is present are :

1.	Cyanides	—CN
2.	Isocyanides	—NC
3.	Nitro compounds	$—NO_2$
4.	Amines	$—NH_2$ (primary)
		>NH (secondary)
		$—\overset{\mid}{N}—$ (tertiary)

9.2. CYANIDES AND ISOCYANIDES

Cyanides can be considered as derivatives of hydrogen cyanide, HCN, obtained by replacing the hydrogen by an alkyl or aryl group. The functional group for this class of compounds is —CN. The cyanide group is known as **ambident** group as it can be attached to the alkyl or aryl radical through either the carbon or the nitrogen atom. When the alkyl group is attached to the carbon atom of the —CN group, the compound is called cyanide ; its attachment to the nitrogen atom leads to isocyanides. Both types of compounds contain multiple bonds.

$$\underset{\text{Cyanide}}{R—C\equiv N} \qquad\qquad \underset{\text{Isocyanide}}{R—N \rightleftarrows C}$$

Cyanides and isocyanides, because of the same molecular formula, are isomeric compounds.

9.2.1. Nomenclature

Nitriles usually derive their names from the carboxylic acid which they would yields on hydrolysis. Thus CH_3CN is acetonitrile (hydrolysis produces acetic acid), CH_3CH_2CN propanonitrile (hydrolysis yields propanoic acid) and C_6H_5CN benzonitrile. Here, the ending 'ic acid' of an acid has been replaced by '—nitrile'.

Alternately, these compounds may be called methyl, prop-1-yl, and phenyl cyanide respectively. In these names the word 'cyanide' is added as a suffix to the corresponding alkyl or aryl group. Compounds RNC or ArNC are alkyl or aryl isonitriles (or isocyanides).

In the IUPAC system, cyanides are named alkanenitriles. The hydrocarbon is named in the usual way, counting also the carbon atom forming the part of the —CN group and the word 'nitrile' is attached to it. The examples given in Table 9.1 explain the system of naming.

TABLE 9.1

Molecular formula	*Trivial name*	*IUPAC name*
CH_3CN	Methyl cyanide or acetonitrile	Ethanenitrile
CH_3CH_2CN	Prop-1-yl cyanide or propanonitrile	Propanenitrile
C_6H_5CN	Phenyl cyanide or benzonitrile	Benzonitrile
$CH_2{=}CHCN$	Vinyl cyanide or acrylonitrile	2-Propenenitrile

9.2.2. Preparation

(*i*) **From acid amides**. Acid amides on dehydration yield nitriles. The commonly used dehydrating agents are phosphorus pentoxide and thionyl chloride. The cyanide so produced is pure, without any contamination with isocyanide.

$$CH_3CONH_2 \xrightarrow{P_2O_5/SOCl_2} CH_3CN + H_2O$$

$$C_6H_5CONH_2 \xrightarrow[-H_2O]{P_2O_5/SOCl_2} C_6H_5CN$$

This is the general method. Both alkyl and aryl nitriles can be obtained by this method. Higher molecular mass amides may be dehydrated by heating alone.

(*ii*) **Form alkyl halides.** Reaction of alkyl halides with inorganic cyanides lead to products which depend upon the inorganic cyanide used. Reaction of alkyl halide with sodium or potassium cyanide in aqueous ethanolic solution gives largely cyanides. However, isocyanides are obtained on reaction with silver cyanide. The cyanide group is a nucleophile. It can attack from both the carbon or the nitrogen atoms, and therefore, called an 'AMBIDENT NUCLEOPHILE'. However, as aryl halides do not undergo ready nucleophilic substitution, aryl cyanides cannot easily be prepared by this method.

$$RX + NaCN \text{ or } KCN \longrightarrow \underset{\text{major}}{RCN} + \underset{\text{minor}}{RNC}$$

$$RX + AgCN \longrightarrow \underset{\text{major}}{RNC} + \underset{\text{minor}}{RCN}$$

This method is of no use for the preparation of aromatic compounds.

(*iii*) **From diazonium salts.** Aryl cyanides can, however, be prepared by the reaction of diazonium salts with copper (I) cyanide and sodium or potassium cyanide (KCN+CuCN).

$$ArN_2^+X^- + CN^- \xrightarrow{KCN+CuCN} ArCN + N_2 + X^-$$

This method is not suitable for the preparation of alkyl cyanides as alkyldiazonium salts are very unstable and cannot be readily obtained.

(*iv*) **Carbylamine reaction.** This reaction is useful for the preparation of isocyanides only. A primary amine is heated with chloroform in the presence of alcoholic sodium hydroxide.

$$CH_3-N\begin{matrix}\diagup H\\ \diagdown H\end{matrix} + \begin{matrix}Cl\diagdown\\ Cl\diagup\end{matrix}C\begin{matrix}\diagup H\\ \diagdown Cl\end{matrix} + 3KOH \longrightarrow CH_3NC + 3KCl + 3H_2O$$

This method establishes that the alkyl radical in isocyanides is directly linked to N atom.

(*v*) **Dehydrogenation of higher amines.** Vapour of amines when passsd over a copper or nickel catalyst at higher temperature yield corresponding nitriles.

$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{N}}}} \xrightarrow[573K]{\text{CU}} RC\equiv N + 2H_2$$

(*vi*) **Industrial method.** Ammonium salts of carboxylic acids dehydrate first to form amide which on losing a water molecule yield nitrile. To manufacture nitriles, carboxylic acid vapours mixed with ammonia are passed over heated alumina of 773 K.

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow R-\overset{\displaystyle O}{\overset{\|}{C}}-O^-NH_4^+ \xrightarrow[773\text{ K}]{Al_2O_3} R-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2$$

$$\downarrow$$

$$R-C\equiv N$$

9.2 3. Physical Properties

The lower alkyl cyanides (up to C_{14}) are colourless liquids with pleasant odour. The higher members are crystalline solids. They are moderately soluble in water but their solubility falls with the

increase of molecular mass. They are readily soluble in organic solvents. Nitriles are not as toxic as compounds containing free CN^- ion. Nitriles are polar compounds with high dipole moment values. They are highly associated molecules, and hence, their boiling points are relatively high.

Alkyl isocyanides are colourless volatile liquids with extremely unpleasant odour. Isonitriles because of intermolecular attractions have high boiling points but lower than the isomeric cyanides. They are only slightly soluble in water and are more poisonous than the cyanides.

9.2.4. Chemical Properties and Reactions

A polar nitrile compound is attacked on both by electrophilic and nucleophilic reagents.

$$R-C\equiv N: \quad \leftrightarrow \quad \underset{\text{Attacked by nucleophile}}{R-\overset{+}{C}} = \underset{\text{Attacked by electrophile}}{\overset{..-}{N}:}$$

Nitriles are not sufficiently basic compounds despite the presence of an unshared pair of electrons at the nitrogen atom. However, they form adition compounds with strong acids in the absence of water.

The important reactions of alkyl cyanides are given below :

(*i*) **Hydrolysis.** Both alkyl cyanides and isocyanides are hydrolyzed by acids or alkalis but the products are different.

$$RCN \xrightarrow[HOH]{H_3O^+} R-CONH_2 \xrightarrow[HOH]{H_3O^+} \underset{\text{(Forms a salt with aqueous acid)}}{RCOOH+NH_3}$$

$$RCN \xrightarrow[HOH]{OH^-} RCONH_2 \xrightarrow[HOH]{OH^-} RCOO^- + NH_3$$

Under acidic conditions, isocyanides yield primary amines and formic acid.

$$RNC \xrightarrow[HOH]{H_3{}^+O} \underset{\substack{\text{Primary amine} \\ \text{(Forms a salt with} \\ \text{aqueous acid)}}}{RNH_2} + HCOOH$$

Aqueous alkali (hot) does not affect isonitriles.

If hydrolysis is carried out with alkaline hydrogen peroxide, (mild conditions), the hydrolysis may be stopped at the amide stage.

Note that the nitrile carbon atom remains attached to the main carbon skeleton when the nitrile is hydrolyzed, whereas the

nitrogen atom remains attached in the isonitrile hydrolysis. Thus —CN group is not completely removed during hydrolysis and therefore alcohols are not produced.

$$\underbrace{RCN + H_2O \longrightarrow ROH + HCN}_{\text{are not the products}}$$

Examples

$$CH_3CN + 2H_2O \longrightarrow CH_3COOH + NH_3$$

$$C_2H_5N \rightleftarrows C + 2H_2O \longrightarrow C_2H_5NH_2 + HCOOH$$

(*ii*) **Reduction.** The carbon-nitrogen triple bond in nitriles can be reduced completely either catalytically by hydrogen in the presence of platinum or nickel or chemically by lithium aluminium hydride. In each case the product is a primary amine.

$$RCN + H_2 \xrightarrow{Pt/Ni} RCH_2NH_2$$

$$RCN + LiAlH_4 \longrightarrow RCH_2NH_2$$

Similarly, reduction with sodium and alcohol gives primary amines.

$$CH_3-C\equiv N + 4[H] \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$$

Reduction with $SnCl_2$ gives aldehyde.

$$RC\equiv N + 2[H] \xrightarrow{SnCl_2} RCH=NH \xrightarrow{H_2O} RCHO$$

Isocyanides on reduction give N-methylamines.

$$R-NC + 2H_2 \xrightarrow{\text{Pt or Ni}} \underset{\text{N-Methyl alkylamine}}{RNHCH_3}$$

This reaction is of little preparative significance, but demonstrates the presence of an R—N linkage in the isonitrile.

(*iii*) **Rearrangement :** When alkyl isocyanides are heated for a long time they rearrange to the cyanice.

$$R-NC \longrightarrow RCN$$

9.2.5. Uses

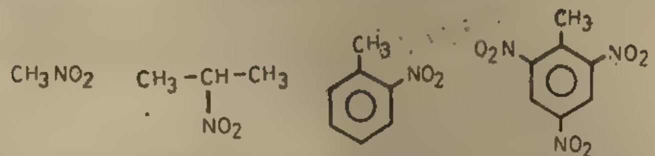
Conversion of an alkyl halide to a cyanide results in the increase of one carbon atom in the molecule (stepping up). As cyanides on reduction can be converted to amines, amides and acids with increasing number of C atoms in the chains, this provides a method for increasing the chain. Cyanides are, thus, useful intermediates in organic synthesis. Acetonitrile is a useful solvent. Acrylonitrile, $CH_2=CHCN$ is used widely in the manufacture of polymers nitrile rubbers and textiles (Unit-15). Thus nitriles are industrially important compounds.

9.3. NITRO COMPOUNDS

Nitro compounds contain the functional group $—NO_2$ (or $-N\begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$), and are obtained by substituting the nitro group for a hydrogen atom in hydrocarbons. Nitro compounds should not be confused with the structurally isomeric nitrite esters which contain no C—N bond (*e.g.*, nitroethane has the structure $CH_3\,CH_2N\begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$, whereas the structure of ethyl nitrite is $CH_3\,CH_2—O—N{=}O$)

9.3.1. Nomenclature

In naming the nitro compounds, term 'nitro' is prefixed to the corresponding hydrocarbon, be it an aliphatic or aromatic one, *e.g.*,



Nitromethane | 2-Nitropropane | 2-Nitrotoluene (o-Nitrotoluene) | 2,4,6-Trinitro toluene (TNT)

9.3.2. Preparation

The chief methods for the preparation of nitro compounds are as follows :

(*i*) **Nitration of alkyl halides.** Alkyl halides (especially iodides) react with metal nitrite to give nitro compounds by nucleophilic substitution. The nucleophile is the NO_2^- ion, which is an ambident nucleophile like the cyanide ion. With silver nitrite the main products are nitro compounds (attack via N) but with sodium (or potassium) nitrite isomeric nitrite esters are usually obtained as well.

$$RI + AgNO_2 \longrightarrow R—NO_2 + AgI$$
$$RI + NaNO_2 \longrightarrow RONO + RNO_2 + NaI$$

These can usually be separated quite easily, though. By using dimethyl sulphoxide (DMSO) as the solvent, the main product is the nitrocompound even by use of sodium nitrite.

$$RI + NaNO_2 \xrightarrow{DMSO} RNO_2 + NaI$$

Aromatic nitro compounds cannot be prepared by this method. It is also not suitable for large-scale preparation of nitro compounds.

A better synthesis is one employing a halogenated carboxylic acid rather than a simple alkyl halide. The carboxylic acid grouping is lost during the reaction, and the product is a simple nitroalkane, *e.g.*

$$NaNO_2 + Cl\,CH_2\,COOH \longrightarrow KCl + CH_3\,NO_2 + CO_2$$

(*ii*) **Direct nitration of hydrocarbons**. Both aliphatic and aromatic nitro-compounds are generally obtained by the direct nitration of the parent hydrocarbon. Aliphatic hydrocarbons do not undergo nitration easily.

To prepare nitroalkanes, vapour phase nitration with nitric acid (or axides of nitrogen) is carried out at high temperatures. A mixture of products is obtained which can be separated by fractional distillation.

$$CH_3-CH_2-CH_3 \xrightarrow[675\,K]{HNO_3} \overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-NO_2 \quad \text{1-Nitropropane}$$

$$+$$

$$\overset{3}{C}H_3-\underset{\displaystyle NO_2}{\overset{2}{C}H}-\overset{1}{C}H_3 \quad \text{2-Nitropropane}$$

$$+$$

$$\overset{2}{C}H_3-\overset{1}{C}H_2-NO_2 \quad \text{1-Nitroethane}$$

$$+$$

$$CH_3-NO_2 \quad \text{Nitromethane}$$

$$+ \text{ alcohols, aldehydes, acids, } CO, CO_2, \textit{etc.}$$

Since nitric acid is an oxidizing agent, a number of oxidation products like alcohols, aldehydes, ketones, acids, carbon monoxide, carbon dioxide, *etc.*, are also obtained. Inspite of all this it is an industrially used process.

Aromatic nitro-compounds are usually prepared by treatment with nitric acid or with nitrating mixture (conc. H_2SO_4+conc. HNO_3).

$$C_6H_5\boxed{H + HO}NO_2 \xrightarrow{H_2SO_4} C_6N_5NO_2 + H_2O$$

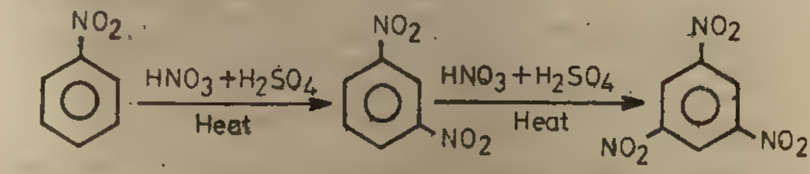
Nitrobenzene

The sulphuric acid promotes the reaction by taking up water and thus protecting the nitric acid from dilution, and also by acting as a catalyst. Nitration in sulphuric acid is due to the production of nitronium ion, NO_2^+ (as electrophile) which is, in fact, the active nitration agent.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Crystalline salts of the nitronium ion are known, *e.g.*, $NO_2^+.ClO_4^-$; $NO_2^+NO_3^-$ (solid N_2O_5) and its existence has been confirmed by physical methods.

To introduce a second and a third nitro group in the nucleus, mixture of fuming nitric acid and concentrated (or fuming) sulphuric acid at elevated temperatures is used. Thus :



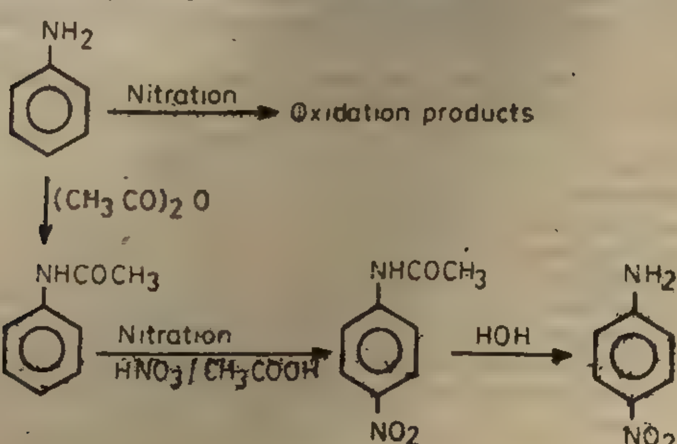
Nitrobenzene m-Dinitrobenzene s-Trinitrobenzene

This is an example of electrophilic aromatic substitution. As can be expected, electrophilic substitutions are facilitated by the presence of electron-donating groups like —OH, —OR, —NH_2 and R (activating substituents) in the aromatic ring and are made more difficult by electron-withdrawing groups like —X, —CN, —COR, —CO_2H and —NO_2 (deactivating substituents).

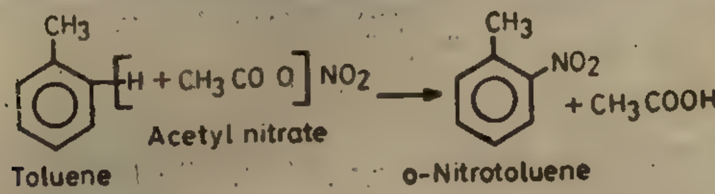
$$HONO_2 + H_2SO_4 \longrightarrow H_2O^+NO_2 + HSO_4^-$$
$$H_2O^+NO_2 \longrightarrow NO_2^+ + H_2O$$

Wheland intermediate

Since nitric acid is an oxidizing agent, sensitive groups like —NH_2 (*e.g.*, in aniline) should be protected, *e.g.*, by acetylation. The protecting group can be removed later.



Action of acetyl nitrate. In certain cases, acetyl nitrate is used as a nitrating agent with an advantage of introducing only one nitro group in the ortho position. Thus :



The use of acetyl nitrate is dangerous, since it tends to explode when heated.

Not more than three nitro groups can usually be introduced into the benzene nucleus. The actual number of nitro groups introduced depends on temperature, nature of the nitrating agent and the nature of the substance to be nitrated.

9.3.3. Physical Properties

Nitroalkanes are colourless volatile liquids of agreeable odour. They are sparingly soluble in water but readily dissolve in organic solvents. They are highly polar compounds and have higher boiling points than the hydrocarbons of comparable molecular masses. Nitroparaffins distil smoothly whereas the isomeric alkyl nitrites explode on heating.

Aromatic nitrocompounds :

1. Aromatic nitro compounds are having pleasant sweetish odours. Some other nitrocompounds like nitrobenzene are pale yellow liquids colourless crystalline solids with no odour.

Nitrobenzene has the smell of bitter almonds, similar to that of benzaldehyde. Nitrobenzene is poisonous.

2. They are heavier than and insoluble in water but dissolve readily in organic solvents such as benzene and alcohol. They are steam volatile and toxic compounds.

3. The mono- di-, and trinitro derivatives of benzene and toluene have progressively higher melting and boiling points.

	mp/K	*bp*/K
Benzene	278·5	353
Nitrobenzene	278·7	484
m-Dinitrobenzene	364	576
s-Trinitrobenzene	395	—
o-Nitrotoluene	276	495
m-Nitrotoluene	289	506
p-Nitrotoluene	325	511

4. When heated strongly, polynitrocompounds detonate with explosive violence and cannot, therefore be distilled under atmospheric pressure.

9.3.4. Chemical Properties and Reactions

1. **Reduction.** The most important reaction of nitrocompounds is their reduction to the corresponding amines. This is done either under acidic conditions by nascent hydrogen or by catalytic hydrogenation :

$$C_2H_5NO_2 \xrightarrow[+HCl]{Sn\ or\ Fe} \underset{\text{Ethylamine}}{C_2H_5.NH_2}$$

$$C_2H_5NO_2 \xrightarrow{Ni/H_2} \underset{\text{Ethylamine}}{C_2H_5.NH_2}$$

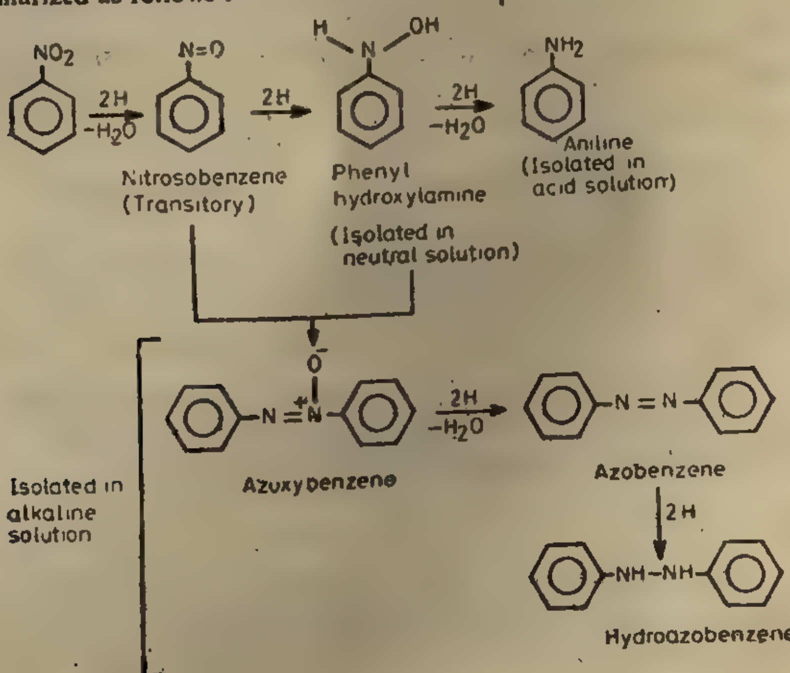
$$C_2H_5NO_2 \xrightarrow[\text{(Neutral)}]{Zn/NH_4Cl} \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH}$$

Lithium aluminium hydride also reduces the nitro compounds.

$$RNO_2 + 6\,[H] \longrightarrow RNH_2 + 2H_2O$$

Under neutral conditions (*e.g.*, with zinc dust and NH_4Cl) reduction proceeds only to hydroxylamines.

Aromatic nitro compounds, however, give complex reduction products depending upon the conditions. The various products obtained from nitrobenzene including the intermediates are summarized as follows :



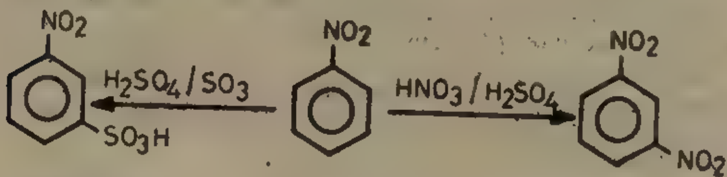
All these products can be reduced to aniline when strong reducing agents, *e.g.*, Sn/HCl are used.

(*ii*) **Hydrolysis**. Hydroxylamine is liberated when a primary nitroalkane is hydrolyzed by acid. This is a disproportionation reaction in which the $-CH_2$ group is oxidized while the $-NO_2$ group is reduced.

$$\underset{}{RCH_2NO_2+H_2O+HCl} \longrightarrow \underset{\substack{\text{Hydroxylamine}\\\text{(as salt)}}}{NH_2OH.HCl}+RCOOH$$

This reaction is now used for the manufacture of hydroxylamine.

(*iii*) **Aromatic substitution**. Electrophilic substitution of nitrobenzene is much more difficult than benzene and substitution occurs at the meta position.



Nitrobenzene is not affected by oxidizing and hydrolyzing reagents.

9.3.5. Uses

The lower nitroalkanes are used as industrial solvents for oils, fats, resins, dyes and cellulose esters and as intermediates in the manufacture of explosives, dyestuffs and detergents. Nitroarenes are important intermediates for the manufacture of a wide variety of aromatic compounds for use in dyestuffs, pharmaceuticals and explosive industries 2, 4, 6-Trinitrotoluene (TNT) and 1, 3, 5-trinitrobenzene are important commercial chemical explosives.

Nitrobenzene is used : (1) for scenting cheap soaps ; (2) in the manufacture of floorand shoe polishes ; (3) as a high boiling solvent ; (4) for the manufacture of aniline and some azo-dyes ; and (5) as an oxidizing agent in organic synthesis.

9.4. AMINES

The amines may be regarded as derivatives of ammonia, in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. They are classified as primary, secondary or tertiary amines according as one, two or three hydrogen atoms of ammonia

are substituted. The substituents in secondary and tertiary amines may or may not be the same. When all the alkyl groups are the same the amine is named as a simple or symmetrical amine and when two or all the three alkyl groups are different the amine is often called mixed or unsymmetrical amine. Thus :

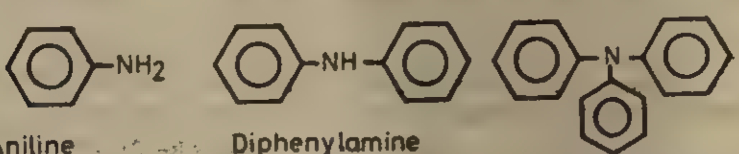
(*i*) Primary amines $\quad R-\underset{\displaystyle H}{\underset{|}{N}}-H$, *e.g.*, Methyl amine $\quad CH_3-\underset{\displaystyle H}{\underset{|}{N}}-H$

(*ii*) Secondary amines $\quad R-\underset{\displaystyle H}{\underset{|}{N}}-R$, *e.g.*, Dimethyl amine $\quad CH_3-\underset{\displaystyle H}{\underset{|}{N}}-CH_3$

(*iii*) Tertiary amines $\quad R-\underset{\displaystyle R}{\underset{|}{N}}-R$, *e.g.*, Trimethyl amine $\quad CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$

A fourth type of compounds called quaternary ammonium salts are obtained by replacement of all the four hydrogen atoms of the ammonium cation by alkyl or aryl substituents, *e.g.*, $(CH_3)_4N^+I^-$, tetramethyl ammonium iodide.

When one or more aryl groups are substituted in place of hydrogen into ammonia, the amine is called an aromatic amine.



Aniline (Primary) $\quad$ Diphenylamine (Secondary) $\quad$ Triphenylamine (Tertiary)

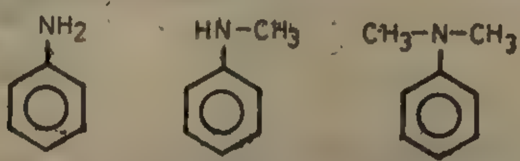
The functional group in three types of amines are, $-NH_2$ group (amino) $>NH$ group (imino) and $\rightarrow N$ group (tertiary nitrogen atom).

9.4.1. Nomenclature

According to the trivial system, simple amines are named after the alkyl groups attached. The suffix of the series is amine. In IUPAC system, either the ending '*e*' of an alkane is replaced by amine or the word amino (or N alkyl amino in case of secondary and N, N-dialkyl amino in case of tertiary amines) is prefixed before the name of the parent compound. At times, the amino group is also considered as substituent and its position on the carbon chain specified by a number. The numbering of the longest chain is done from that end which will give the lowest possible number to the amino group. Both common and IUPAC names of the same amines are given below :

Amine	*Parent hydrocarbon*	*Common name*	*IUPAC name*
CH_3NH_2	CH_3H	Methylamine	Methanamine or Aminomethane
$CH_3CH_2NH_2$	CH_3CH_2H	Ethylamine	Ethanamine or Aminoethane
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2NH_2$	$CH_3CH_2CH_3$	*n*-Propylamine	1-Aminopropane
$\overset{3}{C}H_3\overset{2}{C}H(NH_2)\overset{1}{C}H_3$	$CH_3CH(H)CH_3$	Isopropylamine	2-Aminopropane
CH_3NHCH_3	CH_3-H	Dimethylamine	N-Methylamino-methane
$CH_3N(CH_3)CH_3$	CH_3-H	Trimethylamine	N, N-Dimethyl-aminomethane
$\overset{3}{C}H_3-\overset{2}{C}H(CH_3)-\overset{1}{C}H_2NH_2$	$CH_3-CH(CH_3)-CH_2-H$	Isobutylamine	1-Amino-2 methyl propane
$CH_3-NH-(CH_2)_3CH_3$	$CH_3(CH_2)_2CH_2H$	Butylmethyl amine	1-(N-Methyl amino butane)

Aromatic amines are generally named as derivatives of the simplest aromatic amine, aniline.



Aniline N-Methyl-aniline N,N-Dimethyl-aniline

Aromatic compounds with the aminogroups in the side-chain, *e.g.*, benzylamine, $C_6H_5-CH_2-NH_2$ behave more like aliphatic than aromatic amines.

If the amino group ($-NH_2$) or substituted amino group ($-NHR$ or $-NR_2$) makes a part of the molecule that contains another functional group, the second functional group ($-COOH$, $-OH$, *etc.*) determines the parent name of the compound. For example,

$$\overset{3}{C}H_3-\overset{|}{C}H(H_2N)-\overset{2}{C}H_2\overset{1}{C}OOH$$
3-Amino-1-butanoic acid

$$CH_3-NH-\overset{2}{C}H_2-\overset{1}{C}H_2OH$$
N-Methylamino-1-ethanol

9.4.2. Isomerism

Like other types of organic compounds, amines show **chain isomerism** (different structures of the alkyl groups), *e.g.*,

$$\underset{\text{N-Butyl amine}}{CH_3CH_2CH_2CH_2NH_2} \qquad \underset{\text{Isobutyl amine}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2NH_2}$$

Amines also show **position isomerism** (different placing of amino group), *e.g.*,

$$\underset{\text{1-Aminopentane}}{CH_3-CH_2-CH_2-CH_2-CH_2NH_2} \qquad \underset{\text{3-Aminopentane}}{CH_3CH_2\overset{\overset{NH_2}{|}}{CH}-CH_2CH_3}$$

$$\underset{\text{2-Aminopentane}}{CH_3-\overset{\overset{NH_2}{|}}{CH}-CH_2-CH_2-CH_3}$$

Same molecular formula can also represent all the three types of amines. Thus, C_3H_9N represents the followings amines :

$$\underset{\text{Propylamine}}{CH_3-CH_2-CH_2-NH_2} \qquad \underset{\text{Ethyl methyl amine}}{CH_3-CH_2-NH-CH_3} \qquad \underset{\text{Trimethyl amine}}{CH_3-\overset{\overset{CH_3}{|}}{N}-CH_3}$$

Amines also show metamerism (different alkyl groups bonded to the amine functional group), *e.g.*,

$$\underset{\text{Diethylamine}}{CH_3-CH_2-NH-CH_2CH_3} \qquad \underset{\text{Methyl-}n\text{-propylamine}}{CH_3-NH-CH_2-CH_2-CH_3}$$

$$\underset{\text{Methylisopropylamine}}{CH_3-NH-\overset{\overset{CH_3}{|}}{CH}-CH_3}$$

9.4.3. Preparation of Amines

(*i*) **By treatment of alkyl halides (haloalkanes) with ammonia (ammonolysis) or amines :** When an alkyl halide is treated with the alcoholic solution of ammonia in a sealed tube at 373K, a mixture of substitution products, *i.e.*, primary, secondary, tertiary amines and the quaternary ammonium salt are obtained, which are usually difficult to separate.

$$\underset{\text{Methyliodide}}{CH_3-I} + \underset{\text{Ammonia}}{H-NH_2} \xrightarrow[-HI]{373K} \underset{\substack{\text{Methylamine} \\ \text{(primary)}}}{CH_3NH_2}$$

$$\begin{array}{c} CH_3N-H \\ | \\ H \end{array} + I-CH_3 \xrightarrow[-HI]{373K} (CH_3)_2NH$$

Methylamine — Dimethylamine (secondary)

$$(CH_3)_2N-H+I-CH_3 \xrightarrow[-HI]{373K} (CH_3)_3N$$

Dimethylamine — Trimethylamine (tertiary)

$$(CH_3)_3N+CH_3I \xrightarrow{373K} [(CH_3)_4N^+]I^-$$

Trimethylamine — Tetramethylammonium iodide (quaternary ammonium iodide)

This method is used in the manufacture of amines and not as a laboratory preparation.

However, to obtain primary amines, an excess of ammonia is used.

$$CH_3I \;+\; \underset{\text{(Excess)}}{HNH_2} \longrightarrow \underset{\text{(Main product)}}{CH_3NH_2+HI}$$

To prepare, tertiary amine, an excess of alkyl halide is used. Along with tertiary amine, the quaternary ammonium salt is also obtained.

$$NH_3 \xrightarrow[\text{(Excess)}]{CH_3I} (CH_3)_3N+[(CH_3)_4N]^+I^-$$

The reaction mixture is made alkaline and distilled, when the tertiary amine is obtained. The residual quaternary salt on distilling in vacuo yields more of tertiary amine.

$$[(CH_3)_4N^+]I^- \longrightarrow (CH_3)_3N+CH_3I$$

Primary alkyl halides and the secondary alkyl halide, isopropyl bromide undergo this type of substitution reaction. All other secondary and tertiary halides undergo elimination to give alkenes.

$$\underset{\text{(Excess)}}{CH_3CH_2I+NH_3} \longrightarrow \underset{\text{(Amine)}}{CH_3-CH_2-NH_2}+HI$$

$$\underset{\text{tert-Butyliodide}}{\begin{array}{c} CH_3 \\ | \\ CH_3-C-I \\ | \\ CH_3 \end{array}} + NH_3 \longrightarrow \underset{\text{(Alkene)}}{\begin{array}{c} CH_3 \\ | \\ CH_3-C \\ \| \\ CH_2 \end{array}} + NH_4I$$

Tertiary amines can also be prepared by decomposing the tetramethyl ammonium hydroxide upon heating strongly. First this compound is prepared from $(CH_3)_4N^+I^-$. For example :

$$\underset{\text{Tetramethyl ammonium iodide}}{\begin{array}{c} CH_3 \\ | \\ CH_3-N^+-CH_3\ I^- \\ | \\ CH_3 \end{array}} \xrightarrow[-AgOH]{\text{Moist silver oxide}} \underset{\text{Tetramethyl ammonium hydroxide}}{\begin{array}{c} CH_3 \\ | \\ CH_3-N^+-CH_3\bar{O}H \\ | \\ CH_3 \end{array}} + AgI$$

$$\xrightarrow{\text{Heat}} \underset{\text{Trimethylamine}}{\begin{array}{c} CH_3 \\ | \\ CH_3-N+CH_3OH \\ | \\ CH_3 \end{array}}$$

In these reactions, ammonia and amines act as nucleophiles due to the presence of a lone pair of electrons on the nitrogen atom. Nucleophilic substitution of an alkyl halide by such molecules leads to amines.

(*ii*) **Reduction of nitro compounds, nitriles (cyanides) amides and oximes:** Nitro and nitrile compounds are mainly used for the preparation of primary aromatic amines. Thus, aniline is prepared in the laboratory by reduction of nitrobenzene with tin (or iron or zinc) and hydrochloric acid.

$$\underset{\text{Nitrobenzene}}{C_6H_5-NO_2}+6[H] \xrightarrow{Sn/HCl} \underset{\text{Aniline}}{C_6H_5-NH_2}+2H_2O$$

Aniline is prepared industrially, using iron and steam.

The reduction may also be carried out catalytically with hydrogen in the presence of nickel or platinum.

$$C_6H_5NO_2 \xrightarrow{H_2(\text{Pt or Ni})} C_6H_5NH_2$$

$$C_2H_5NO_2 \xrightarrow{H_2(\text{Pt or Ni})} C_2H_5NH_2$$

Reduction of nitroalkanes with tin and hydrochloric acid, or with hydrogen and nickel catalyst also give mainly primary amines.

$$\underset{\text{Nitro-ethane}}{C_2H_5NO_2}+3H_2 \longrightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2}+2H_2O$$

This method is becoming increasingly important as more nitro-alkanes are being made available by the vapour phase nitration.

Mostly primary amines are obtained from cyanides by catalytic hydrogenation or reduction with nascent hydrogen (**Mendius reaction**).

$$\underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[Na/C_2H_5OH]{H_2/Pt} \boxed{+4[H]} \rightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

Secondary amines are obtained by similar reduction but of isocyanides.

$$\underset{\text{Methyliso-cyanide}}{CH_3NC} \xrightarrow{H_2/Ni \text{ or } +4[H]} \underset{\text{Dimethyl amine}}{CH_3NHCH_3}$$

Amides on reduction also give primary, secondary and tertiary amines depending upon the nature of amide.

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[Na/C_2H_5OH]{H_2/Pt} \boxed{+4[H]} \rightarrow \underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2} + H_2O$$

N-substituted amides on reduction with lithium aluminium hydride or other reducing agents, *e.g.*, sodium and ethanol, hydrogen in the presence of metal catalyst, give secondary and tertiary amines.

$$\underset{\text{N-alkyl amide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R'} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Secondary amine}}{R-CH_2-NHR'} + H_2O$$

$$\underset{\text{N, N-Dialkyl amide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-N\begin{matrix} \diagup R' \\ \diagdown R' \end{matrix}} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Tertiary amine}}{R-CH_2-N\begin{matrix} \diagup R \\ \diagdown R' \end{matrix}} + H_2O$$

Oximes of aldehydes and ketones on reduction with sodium and alcohol also give primary amines.

$$\underset{\text{Acetaldoxime}}{CH_3CH{=}NOH} \xrightarrow[Na/C_2H_5OH]{+4[H]} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

$$\underset{\text{Acetoxime}}{(CH_3)_2C{=}NOH} \xrightarrow[Na/C_2H_5OH]{+4[H]} \underset{\text{Isopropylamine}}{(CH_3)_2CHNH_2}$$

Lithium aluminium hydride can also be employed as a reducing agent to prepare amines from the above classes of compounds.

(*iii*) **Hofmann bromamide reaction (Hofmann degradation)** : Primary amides (*i.e.*, $RCONH_2$) on treatment with bromine and alkali give amines.

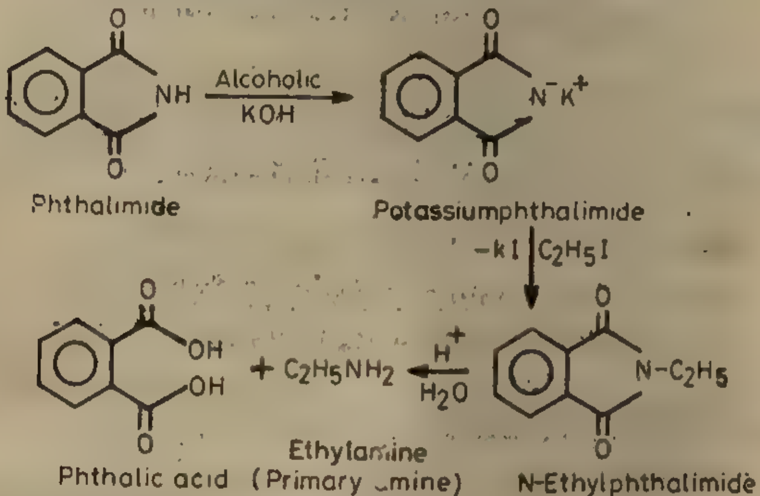
$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

This method yields primary amines only. It is important to note that the amide has lost one carbon atom. This method is, thus, a means of stepping down the series, since the amine contains one carbon less than the amide.

(*iv*) **Other methods**

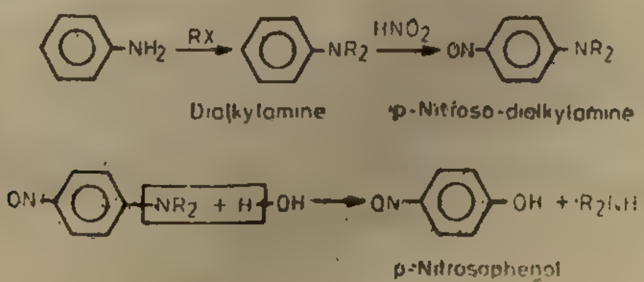
1. **Gabriel's Phthalimide Method** (Gabriel, 1887). According to this method the treatment of potassium phthalimide with alkyl halide forms alkylphthalimide which on hydrolysis with hydrochloric acid gives pure primary amine.

This is because phthalimide the reagent used in this synthesis has only one replaceable hydrogen so that only one R group is introduced, and therefore, pure primary amine is obtained.



This is one of the best methods for the preparation of primary amines.

2. **Hydrolysis of p-Nitroso-dialkylanilines.** The desired compound is prepared by heating aniline with the appropriate alkyl halide followed by nitrous acid. The p-nitrosodialkylaniline so obtained on boiling with sodium hydroxide yields a secondary amine.



This is an excellent method for the preparation of secondary amines.

3. **Methods of Preparation of Tertiary Amines.** They are best prepared by heating the corresponding quaternary ammonium hydroxide which is conveniently obtained by the action of moist silver oxide on the quaternary iodide.

$$\underset{\text{Tetramethyl-ammonium iodide}}{(CH_3)_4NI} + AgOH \longrightarrow \underset{\text{Tetramethyl-ammonium hydroxide}}{(CH_3)_4NOH} + AgI$$

$$(CH_3)_4NOH \xrightarrow{\text{Heat}} \underset{\text{Trimethyl-amine}}{(CH_3)_3N} + CH_3OH$$

(*v*) **Industrial preparations.** The industrial preparation of important amines are given below :

1. **Ethyl amine, diethyl amine and triethyl amine.** A mixture of these three is obtained by passing vapours of alcohol and ammonia over a heated catalyst (Al_2O_3 or ThO_2); ethyl amine may be obtained as the main product by using a large excess of ammonia. This method is called ammonolysis of alcohols.

$$C_2H_5{-}OH + H{-}NH_2 \xrightarrow[723K]{\text{Alumina}} \underset{\text{Ethylamine}}{C_2H_5{-}NH_2} + H_2O$$

$$C_2H_5NH{-}H + HO{-}C_2H_5 \longrightarrow \underset{\text{Diethylamine}}{(C_2H_5)_2{-}NH} + H_2O$$

$$(C_2H_5)_2N{-}H + HO{-}C_2H_5 \longrightarrow \underset{\text{Triethylamine}}{(C_2H_5)_3N} + H_2O$$

Methylamine dimethylamine and trimethylamine may be manufactured by using methanol and ammonia.

In general

$$RH + NH_3 \xrightarrow{Al_2O_3} RNH_2 + R_2NH + R_3N_4 \;(R = CH_3, NC_2H_5)$$

2. **Aniline.** Aniline is manufactured by three processes :

(*i*) **By the reduction of nitrobenzene with scrap iron and steam in the presence of small amount of hydrochloric acid :**

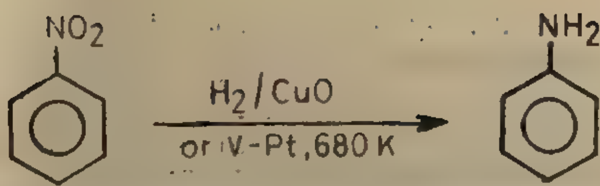
$$Fe + 2HCl \longrightarrow FeCl_2 + 2[H]$$

$$\underset{\text{Nitrobenzene}}{C_6H_5{-}NO_2} + 6[H] \longrightarrow \underset{\text{Aniline}}{C_6H_5{-}NH_2} + 2H_2O$$

The acid helps releasing hydrogen from steam. The hydrochoric acid is regenerated by hydrolysis of ferrous chloride.

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$

(*ii*) Aromatic amines like aniline are produced commercially by vapour phase reduction of nitrobenzene with hydrogen using copper oxide or vanadium-platinum as catalyst.



(iii) **By the action of ammonia on chlorobenzene under pressure.** Aniline is manufactured from chlorobenzene by heating at 473K, under pressure, with ammonia in the presence of cuprous oxide catalyst.

$$\underset{\text{Chlorobenzene}}{2C_6H_5Cl}+2NH_3+Cu_2O \xrightarrow[50\text{ atm}]{473K} \underset{\text{Aniline}}{2C_6H_5NH_2}+2CuCl+H_2O$$

Some methods of preparing amines are summarized in Fig 9.1.

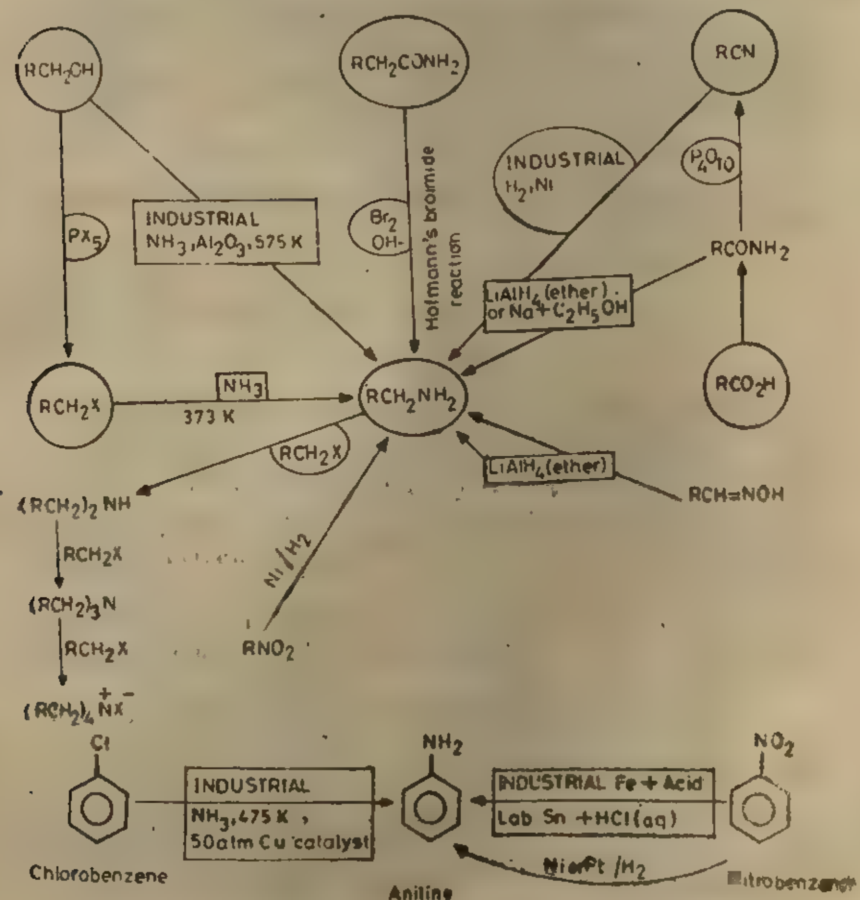


Fig. 9.1. Methods of preparing aliphatic and aromatic amines

9.4.4. Physical properties

Among alkylamines the lower ones are gases with smell of ammonia As the molecular mass increases, these become liquids and finally solids. They have fishy smell. Lower arylamines are either liquids with unpleasant small or low melting solids.

Like ammonia, amines are polar compounds and are united by intermolecular hydrogen bonds.

$$\begin{array}{ccccc} & \text{R} & & \text{R} & & \text{R} & \\ & | & & | & & | & \\ \cdots & \text{N—H} & \cdots\cdots & \text{N—H} & \cdots\cdots & \text{N—H} & \cdots \\ & | & & | & & | & \\ & \text{H} & & \text{H} & & \text{H} & \end{array}$$

Tertiary amines do not show H-bonding.

Amines, therefore, have higher boiling points than corresponding hydrocarbons. The boiling points are, however, lower than corresponding alcohols and carboxylic acids because the hydrogen bonds in amines are weaker (nitrogen is less electronegative than oxygen). Thus, the bp decreases in the order

$$R—CH_2—NH_2 < R—CH_2OH < R—CO_2H$$

All the three types of amines are capable of forming hydrogen bonds with water.

$$\begin{array}{ccccccccccc} & \text{R} & & \text{H} & & \text{R} & & & & \text{R} & \\ & | & & | & & | & & & & | & \\ \cdots & \text{N—H} & \cdots & \text{O—H} & \cdots & \text{N—H} & \cdots & \text{O—H} & \cdots\cdots & \text{N—H} & \cdots \\ & | & & & & | & & | & & | & \\ & \text{H} & & & & \text{H} & & \text{H} & & \text{H} & \end{array}$$

The lower aliphatic amines, thus become water soluble. The solubility of higher amines in water decreases with increase of bulk of alkyl group. They are, however, readily soluble in organic solvents.

Aromatic amines are insoluble in water but soluble in benzene, ether and alcohol. They are volatile in steam, and can be distilled without decomposition.

They are easily oxidized by air. Aniline, though colourless when pure, is usually slightly coloured. Aromatic amines are appreciably toxic.

Aromatic amines are much weaker bases than alkyl amines and are neutral to litmus.

9.4.4. Chemical Reactions

(*i*) **Basic nature**. Like ammonia, all aliphatic amines are basic in nature. They owe their basic character to the lone pair of electrons on nitrgen and can form strong bonds to protons (Lewis concept).

$$\begin{array}{c} H \\ | \\ R-N: \\ | \\ H \end{array} + H^+ \longrightarrow \begin{array}{c} H \\ | \\ R-N^+-H \\ | \\ H \end{array}$$

The ease with which the lone pair can bond to the porton, and hence the base strength of the compound, depends upon the groups attached tc nitrogen. If the substituent group is electron withdrawing (−I), the base strength is reduced because of its lesser ability to form donor bond with the proton.

An alkyl group adjacent to nitrogen increases the availability of the electrons (+I effect) and so aminoalkanes are stronger bases than ammonia. In case of aryl amines, the basic character is less as the aryl group withdraws electrons from the nitrogen atom.

Typical reactions with water and acids are :

With water. Aliphatic amines dissolve in water forming quaternary ammonium hydroxides, which furnish hydroxyl ions on dissociation.

$$\begin{array}{l} H \diagdown \\ R - N: \\ H \diagup \end{array} + H_2O \longrightarrow \left[\begin{array}{l} H \diagdown \\ R - N^+ - H \\ H \diagup \end{array} \right] OH^- \longrightarrow \begin{array}{l} H \diagdown \\ R - N^+ - H \\ H \diagup \end{array} + OH^-$$

The dissociation constant, K_b of the base (amine) for the above equilibrium is defined as follows :

$$K_b = \frac{[RNH_3]^+ [OH^-]}{[RNH_2] [H_2O]}$$

The higher the value of K_b, the greater the strength of the amine (base).

The value of K_b for ammonia and a few amines are given below :

Base	K_b	*Base*	K_b
NH_3	1.8×10^{-4}	$C_2H_5NH_2$	4.7×10^{-4}
CH_3NH_2	4.2×10^{-4}	$(C_2H_5)_2NH$	9.5×10^{-4}
$(CH_3)_2NH$	5.1×10^{-4}	$(C_2H_5)_3N$	5.5×10^{-4}
$(CH_3)_3N$	0.6×10^{-4}	$C_6H_5NHCH_3$	7.1×10^{-10}
$C_6H_5NH_2$	4.2×10^{-10}	$C_6H_5N(CH_3)_2$	11.0×10^{-10}

With acids. Amines react with acids forming quaternary salts, *e.g.*,

$$CH_3-NH_2 + HCl \longrightarrow NH_3N^+H_2Cl^- \; (CH_3NH_2.HCl)$$

(Methyl ammonium chloride)

even water insoluble amines like aniline are converted into water soluble salts.

$$C_6H_5NH_2 + HCl \longrightarrow \underset{\text{Phenyl ammonium chloride}}{C_6H_5N^+H_3Cl^-}$$

Water insoluble amines can thus be differentiated or separated from other water insoluble compounds by their solubility in dilute mineral acids. All amines are weaker bases than NaOH, and so are released from their salts (as in ammonia) by treating with aqueous alkali.

$$CH_3NH_3{}^+\bar{Cl} + Na\,OH \longrightarrow CH_3NH_2 + H_2O + NaCl$$

These salts are water soluble ionic compounds. They are non-volatile, solid and generally decompose before melting. They are insoluble in non-polar solvents.

Amines react with a number of electrophiles like metal ions, alkyl halides, acid chlorides and acid anhydrides.

(*ii*) **Reaction with metal ions.** Like ammonia, amines also form coordination compounds with metal ions like Ag^+ and Cu^{2+}. Thus, silver chloride dissolves in methylamine solution.

$$\underset{\text{(insoluble)}}{AgCl} + 2CH_3NH_2 \longrightarrow \underset{\text{(soluble)}}{Ag(CH_3NH_2)_2{}^+Cl^-}$$

Similarly, Cu^{2+} also form a deep blue $[Cu(CH_3NH_2)_4]^{2+}$ ion with methylamine. Metal complexes with other amines like 1, 2-diaminoethane and 1, 3-diaminopropane are also known.

(*iii*) **Reactions of amines with alkyl halides (Alkylation).** Like ammonia, amines react with alkyl halides in the basic medium to form the next higher class of amines. Alkyl iodides are better (or more) reactive than chlorides or bromides for this reaction. A primary amine (actually any alkylhalide) is converted by methyl-iodide to a secondary then to a tertiary and finally to a quaternary ammonium salt.

$$CH_3{-}NH_2 \xrightarrow[-HI]{CH_3I} (CH_3)_2NH \xrightarrow[-HI]{CH_3I} (CH_3)_3N \xrightarrow{CH_3I} (CH_3)_4N^+I^-$$

This reaction, which gives the quaternary salt, on treating amine with CH_3I is called '**exhaustive methylation**'. This is used in the Hofmann method for determination of structures of complex amines. Halogenoarenes do not react in this way.

(*iv*) **Reaction with acid chlorides and acid anhydrides (Acylation).** Amines (Aliphatic or aromatic) with replaceable hydrogens (primary and secondary) react with acid anhydrides and acid chlorides to give acid acyl derivatives. A tertiary amine with no replaceable hydrogen does not give this reaction.

Vith acyl halides.

$$\underset{\substack{\text{Primary}\\\text{amine}}}{RNH_2} + \underset{\substack{\text{Acetyl}\\\text{chloride}}}{CH_3COCl} \longrightarrow RNH-\overset{\displaystyle Cl}{\underset{\displaystyle CH}{\overset{|}{\underset{|}{C}}}}-CH_3 \xrightarrow[-HCl]{\text{Base}} \underset{\text{N-alkyl-acetamide}}{RNH-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3}$$

$$\underset{\text{Secondary amine}}{R_2{>}NH} + CH_3COCl \xrightarrow[HCl]{\text{Base}} \underset{\text{N, N-Dialkyl-acetamide}}{R_2{>}N-COCH_3}$$

For example :

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\substack{\text{Benzoyl-}\\\text{chloride}}}{C_6H_5COCl} \xrightarrow[-HCl]{\text{Base}} \underset{\text{N-Phenylbenzamide}}{C_6H_5NHCO\,C_6H_5}$$

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + CH_3COCl \xrightarrow[-HCl]{\text{Base}} \underset{\text{N-Ethyl acetamide}}{C_2H_5NH\,CO\,CH_3}$$

$$\underset{\text{Diethylamine}}{(C_2H_5)_2NH} + CH_3COCl \xrightarrow[-HCl]{\text{Base}} \underset{\substack{\text{N, N-Diethyl}\\\text{acetamide}}}{(C_2H_5)_2NCO\,CH_3}$$

With acid anhydrides :

$$\underset{\substack{\text{Primary}\\\text{amine}}}{RNH_2} + \begin{matrix} CH_3-CO \\ CH_3-CO \end{matrix}{>}O \xrightarrow{\text{Base}} \underset{\text{N-Alkylacetamide}}{R-NH-COCH_3} + CH_3COOH$$

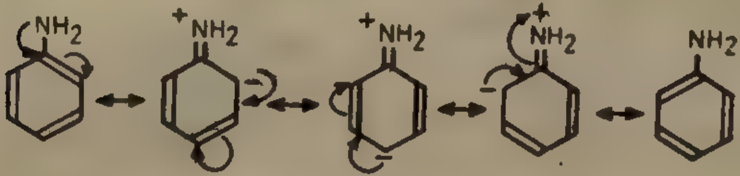
$$\underset{\text{Secondary amine}}{R-NH-R} + \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}{>}O \xrightarrow{\text{Base}} \underset{\text{N, N-Dialkylacetamide}}{R-\underset{\displaystyle COCH_3}{\underset{|}{N}}-R} + CH_3COOH$$

For the removal of HCl or CH_3COOH in the last step the reaction is carried out in the presence of a base like tertiary amine, pyridine or sodium hydroxide. Tertiary amines do not undergo this reaction as they lack a replaceable hydrogen. The acylation with acid anhydride is slower.

The acetyl and benzoyl derivatives are useful for the characterization of primary and secondary amines in the laboratory:

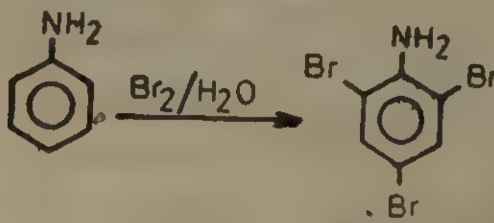
(*v*) **Reactions of the aromatic ring**. Aromatic amines show a number of substitution reactions which are influenced by the amino

group present. The amino group is a srong electron releasing group and activates the para- and the ortho-positions :

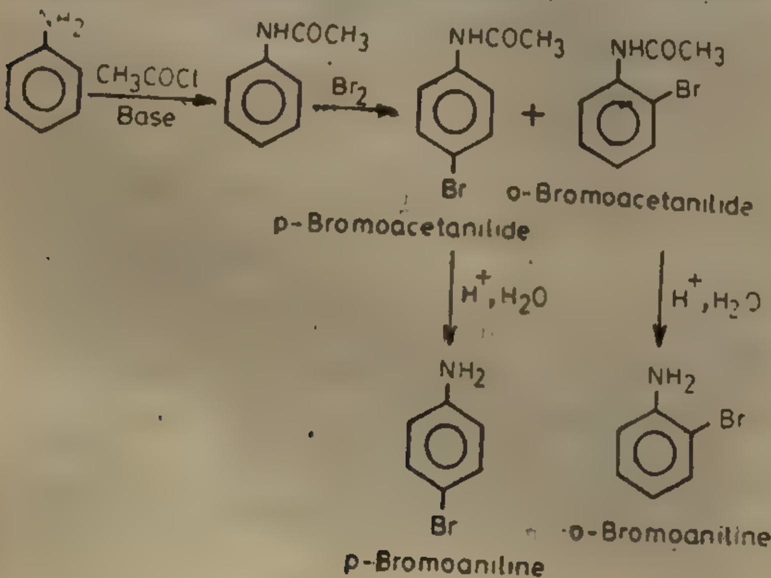


Increased electron density at ortho- and para- position.

1. **Halogenation**. Because of activation of the ring, substitution is quite easy. In fact it is difficult to obtain monosubstituted products. Thus, an aqueous suspension of aniline gives an almost immediate white precipitate of 2, 4, 6-tribromoaniline, when treated with bromine water at room temperature.

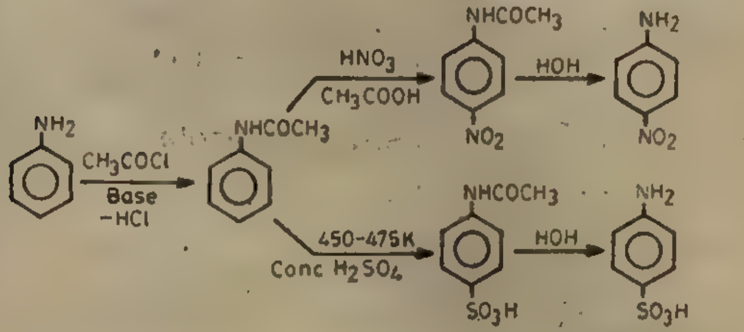


To get a monosubstituted product the activity of the amino group needs to be reduced (*e.g.*, by acetylation) :



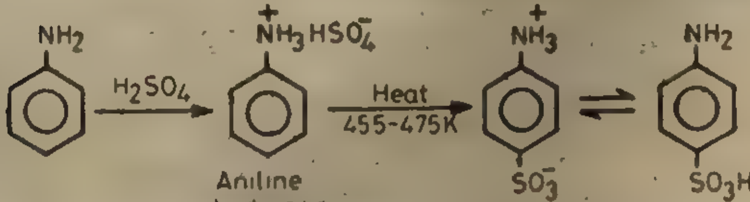
The free amino group is liberated in the last step by hydrolysis.

2. **Nitration and sulphonation.** The amino group in primary aromatic amines (*e.g.*, aniline) is readily oxidized (see above). As the reagents used, both for nitration (either conc. HNO_3 or nitrating mixture), or sulphonation (conc. H_2SO_4) are strong oxidizing agents, it is necessary to protect the amino group before these reactions can be successfully carried out. This is normally done by acetylation. As mentioned under halogenation (above), the acetylated product can be easily hydrolyzed to the amine later :



Sulphanilic acid (p-aminobenzenesulphonic acid) may also be obtained by heating the salt obtained by the reaction of aniline and sulphuric acid :

Aniline forms anilinium hydrogen sulphate with sulphuric acid, which on heating gives sulphanilic acid.

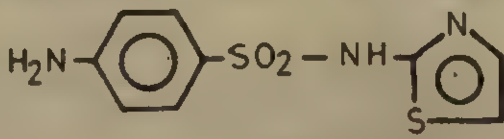


Compounds like sulphanilic acid which contain both an acidic ($-SO_3H$) and a basic ($-NH_2$) groups can exist as internal salts or zwitter ions. Other common examples of zwitter ions are the amino acids, *e.g.*, glycine :

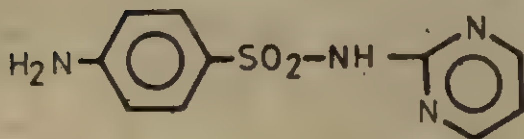
$$\begin{array}{l} CH_2-COO^- \\ | \\ {}^+NH_3 \end{array} \qquad \text{Glycine as zwitter ion}$$

Molecules existing as zwitter ions are characterized by high mp almost total near insolubility in organic solvents, as is common with other ionic solids.

Sulphanilic acid is an important intermediate in the manufacture of dyes and drugs. The well-known antibacterial sulpha drugs like sulphathiazole and sulphadiazine are made from sulphanilic acid derivatives.

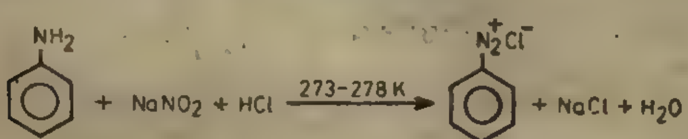


Sulphathiazole



Sulphadiazine

3. **Formation of aromatic diazonium salts** : Aromatic primary amines react readily with nitrous acid at 273-278 K to give arenediazonium salts. These diazonium salts are stable in cold solution, but decompose violently when dry.



Benzene diazonium chloride

The reactions of arenediazonium salts can be divided into two categories : (*a*) substitution reaction, and (*b*) coupling reactions.

(*a*) **In substitution reactions**, nitrogen is lost as N_2 gas and a different group is introduced in its place. Some examples are preparation of hydrocarbons, phenols, arylhalides, cyanides, *etc.*

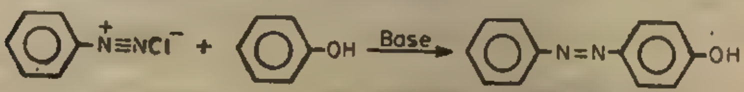
(*i*) $ArN_2X+H_3PO_2+HOH \longrightarrow ArH+N_2+H_3PO_3+HX$

(*ii*) $ArN_2X+HOH \xrightarrow[(H^+)]{\text{Warming}} ArOH+N_2+HX$

$$\left.\begin{aligned}
&(iii)\ ArN_2Cl \xrightarrow{Cu_2Cl_2} ArCl + N_2\\
&(iv)\ ArN_2Cl \xrightarrow{Cu_2Br_2} ArBr + N_2\\
&(v)\ ArN_2X \xrightarrow{CuCN} ArCN + N_2 + X^-
\end{aligned}\right\}\ \text{SANDMEYER REACTION}$$

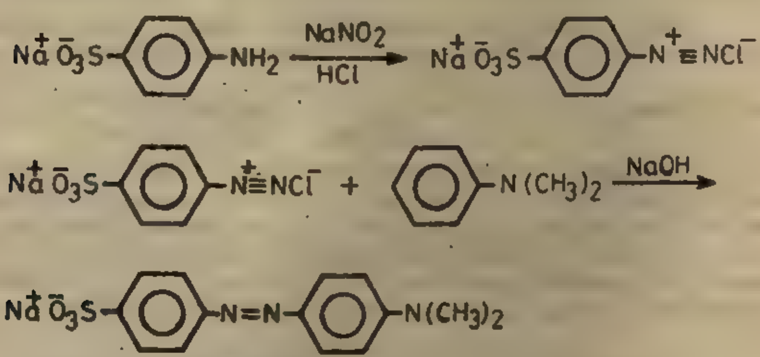
Reactions (*iii*), (*iv*) and (*v*) are known as Sandmeyer reaction.

(*b*) In **coupling reactions**, the diazonium salts react with electron-rich aromatic compounds like phenols and aromatic amines to give azo compounds. Nitrogen is retained in these reactions. These reactions form the basis of azodyes formation.



(Azo compound)
p-Hydroxyazobenzene

For example methyl orange, an azodye indicator, is obtained by coupling the diazonium salt of sulphanilic acid with N, N-dimethylaniline.



Methyl orange

9.4.6. Analysis of Amines

A compound might be an amine if

(*i*) elemental analysis shows the presence of nitrogen.

(*ii*) a water-insoluble compound is soluble in dilute acid.

(*iii*) a water soluble compound turns litmus blue.

To distinguish between primary, secondary and tertiary amines various tests may be performed (Table 9.2) :

Chemistry of the Hinsberg's test

The mixture of amines is treated with benzene sulphonyl chloride, $C_6H_5SO_2Cl$ and excess of aqueous potassium or sodium hydroxide.

A primary amine yields a clear solution which on acidification yields an insoluble sulphonamide. This dissolves in potassium hydroxide, due to the formation of the potassium salt of the enolic sulphonamide.

$$RNH_2 + C_6H_5SO_2Cl \xrightarrow{OH^-} [C_6H_5SO_2\underset{\underset{H}{|}}{N}R] \xrightarrow[-HO_2]{KOH} [C_6H_5SO_2NR]^- K^+ \ \text{(Soluble)}$$

Replaceable hydrogen

$$[C_6H_5SO_2NR]^- K^+ \xrightarrow[\text{Acid}]{H^+} \underset{\text{(Insoluble)}}{C_6H_5SO_2\,NH\,R}$$

A secondary amine yields an insoluble compound unaffected by acid (since it has no replaceable hydrogen):

$$R_2NH + C_6H_5{-}SO_2Cl \xrightarrow{KaOH} \underset{\text{(Insoluble in KOH)}}{C_6H_5SO_2NR_2} \xrightarrow[H+]{\text{NaOH or}} \text{No action}$$

The tertiary amine does not react with benzenesulphonyl chloride.

A tertiary amine yields an insoluble compound (the unchanged amine itself) which dissolves upon acidification of the mixture,

$$R_3N + C_6H_5SO_2Cl \xrightarrow{NaOH} \underset{\text{(Insoluble)}}{R_3N} \xrightarrow{HCl} \underset{\text{(Soluble)}}{R_3N^+HCl^-}$$

The resulting alkaline solution is distilled when the tertiary amine passes over and the residual mixture is filtered; the filtrate on acidification gives the sulphonamide of the primary amine, while the solid residue is the sulphonamide of the secondary amine. The two sulphonamides thus isolated are hydrolyzed with hydrochloric acid to regenerate the individual amines which are distilled off.

$$C_6H_5SO_2\boxed{NHR + H}OH \longrightarrow \underset{\text{Benzene-sulphonic acid}}{C_6H_5SO_2OH} + \underset{\text{Primary amine}}{RNH_2}$$

$$C_6H_5SO_2\boxed{NR_2 + H}OH \longrightarrow C_6H_5SO_2OH + \underset{\text{Secondary amine}}{R_2NH}$$

Now benzenesulphonyl chloride has been replaced by p-toluenesulphonyl chloride, $CH_3C_6H_4SO_2Cl$.

Carbylamine Test

When primary amines are heated with trichloromethane and ethanolic alkali, the foul smelling isonitrile (or carbylamine) is produced.

$$CHCl_3 + 3KOH + CH_3NH_2 \xrightarrow{\text{Warm}} 3KCl + 3H_2O + \underset{\text{Methyl isonitrile}}{CH_3NC}$$

Only the primary amines give this reaction.

Reaction of amines with nitrous acid

Nitrous acid behaves differently than other acids with amines. It is unstable and has to be prepared fresh by dissolving sodium nitrite in dilute hydrochloric acid. Primary, secondary and tertiary amines behave differently. The reaction can thus be used for their differentiation.

(*i*) **Primary amines** having two available H atoms, react with nitrous acid to form primary alcohols with the evolution of nitrogen (Test).

$$\underset{\text{Primary amine}}{RN\boxed{H_2 + O}}\underset{(HNO_2)}{=N-OH} \longrightarrow \underset{\substack{\text{Diazonium}\\\text{salt}\\\text{(Unstable)}}}{RN^+ \equiv NOH^-} \xrightarrow{+H^+} \underset{\text{Carbonium ion}}{R^+} + H_2O + N_2$$

$$\underset{\text{Carbonium ion}}{R^+} \xrightarrow{HO^-} \underset{\text{Alcohol}}{ROH}$$

Primary aromatic amines (*e.g.*, aniline) react to give the stable aromatic diazonium salts. The diazonium salt from aniline is, however, unstable to heat and is hydrolyzed to phenol when heated in water.

$$\underset{\text{Aniline}}{C_6H_5{-}NH_2} \xrightarrow{HNO_2} \underset{\text{(Unstable)}}{C_6H_5N_2^+\,OH^-} \xrightarrow[\text{Warm}]{H_2O} \underset{\text{Phenol}}{C_6H_5OH}$$

The diazonium salts are versatile intermediates, useful for the synthesis of a number of compounds.

Secondary amines : Both aliphatic and aromatic secondary amines react with nitrous acid to produce neutral, yellow oily product, N-nitrosoamines. The lone hydrogen atom present in these amines is replaced by a nitroso group yielding an N-nitroso-compound. Nitrogen is not evolved.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>N{-}\boxed{H+HO}{-}N=O \xrightarrow[-H_2O]{} \underset{\substack{\text{Dimethyl N-nitrosoamine}\\\text{(Carcinogen)}}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>N{-}N=O}$$

$$C_6H_5{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}\boxed{H + HO}{-}N{=}O \xrightarrow[-H_2O]{} C_6H_5{-}\overset{\displaystyle CH_3}{\overset{|}{N}}{-}N = O$$

N-methyl-N-nitrosoaniline

The formation of N-nitrosoamine is used as a test for secondary amines in the Liebermann nitroso reaction. The nitrosoamine on warming with a crystal of phenol and a few drops of concentrated sulphuric acid yields a blue green solution. On dilution the colour changes to red and changes further to deep blue on treatment with alkali.

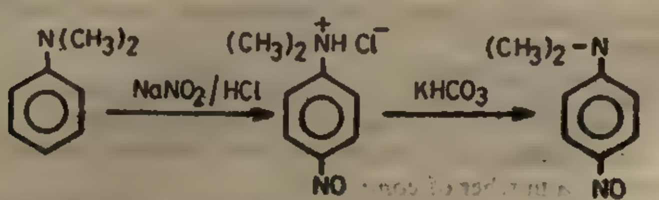
Tertiary amines : With aliphatic tertiary amines only normal acid-base reactions occur as there is no replaceable hydrogen.

$$(CH_3)_3N + HNO_2 \longrightarrow [(CH_3)_3NH]^+ \ NO_2^-$$

Trimethyl ammonium nitrite

The tertiary amine can be regenerated from the salt solution by addition of alkali.

Aromatic tertiary amines undergo electrophilic aromatic substitution by the NO group at the para-position to give water soluble para-nitroso compounds. The introduction of —N=O group in the benzene ring is called nitrosation.



(Orange) (Green)

Differences in behaviour of the three classes of amines with nitrous acid may be used for their distinction.

Tests for aniline

1. Aniline has a characteristic odour.
2. It gives carbylamine reaction.
3. On adding a few drops of potassium dichromate solution

to aniline dissolved in sulphuric acid, a deep blue or black colour is produced.

4. On adding bromine water to an aqueous solution of aniline, a pinkish precipitate is obtained.

5. On adding a solution of bleaching powder to an aqueous solution of aniline, a purple colour is produced.

6. When sodium nitrite is added to an ice-cold solution of aniline in hydrochloric acid followed by a few drops of on alkaline solution of β-naphthol, a brilliant red precipitate is obtained.

Reactions of aliphatic and aromatic amines are summarized in Figs. 9.2 and 9.3. Figure 9.4 suggests the importance of diazonium compounds.

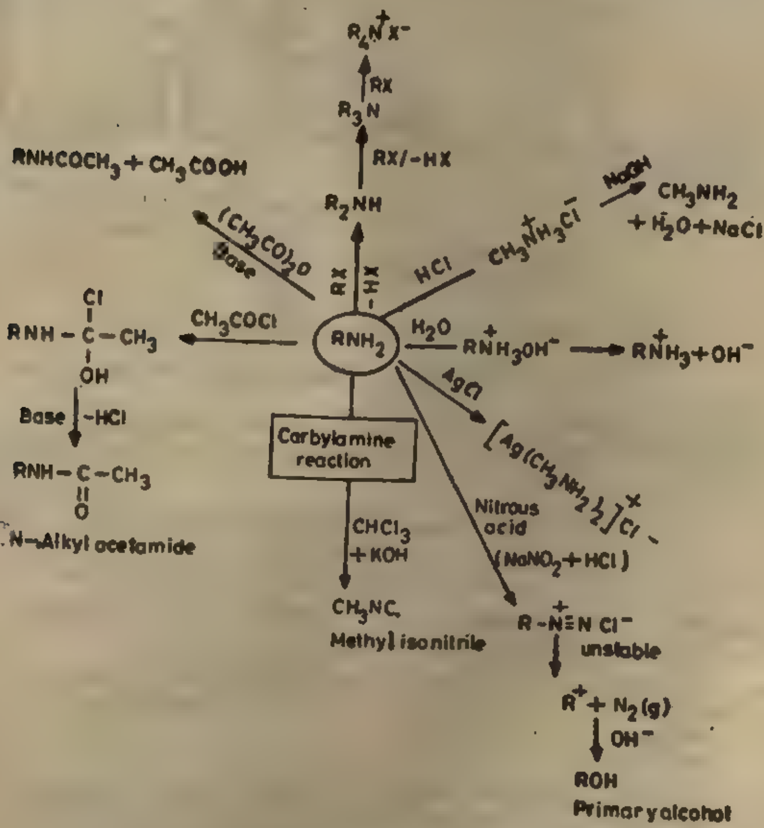


Fig. 9.2. Reactions of aliphatic amines (primary)

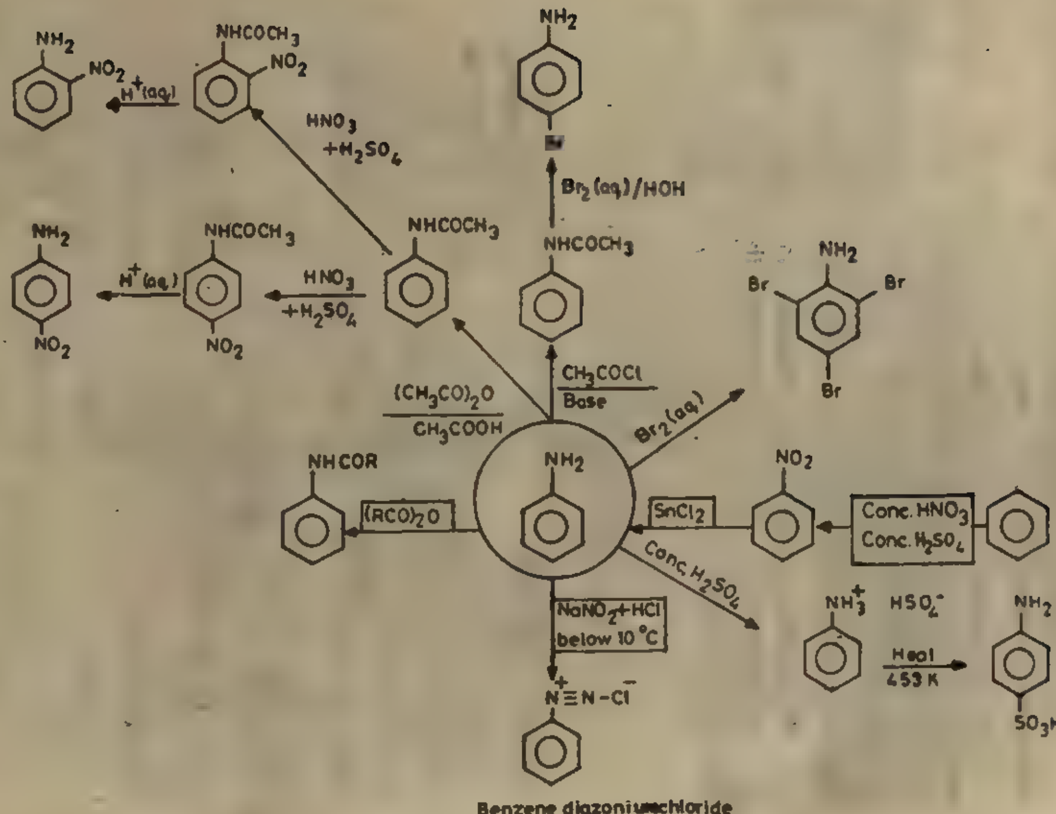


Fig. 9·3. Reactions of aniline

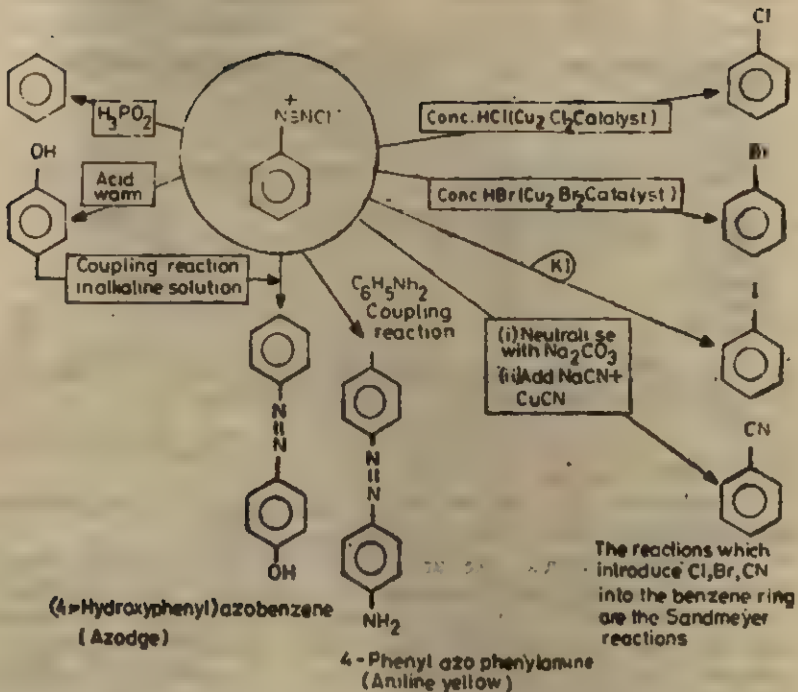


Fig. 9.4. Reactions of benzenediazonium chloride

Distinction between three Classes of Amines

The primary, secondary and tertiary amines can be distinguished from each other on the basis of the following tests. (Table 9.2).

TABLE 9.1. Tests generally employed to differentiate between amines

Reagent	*Primary amine*	*Secondary amine*	*Tertiary amine*
1. Litmus solution	Their aqueous solutions are basic to litmus.	They are more basic than primary [redacted]	They are more basic than secondary amines.
2. Nitrous acid in cold	**Ethylamine**: quantitative evolution of N_2+mixture of alcohol, alkene, *etc.* Cold Aniline : Diazonium salt which gives dye test On warming ; evolution of N_2+phenol	Oily nitrosoamine which answers the Lieberman nitrosoamine test.	**In cold** : form nitrites **In hot** : Complex products

Reagent	*Primary amine*	*Secondary amine*	*Tertiary amine*
3. (*i*) Hinsberg's reagent excess NaOH	Clear solution	Insoluble compound	Insoluble
(*ii*) Acidify	Precipitate appears	Unaffected by acid	Clear solution
4. Chloroform + alcoholic NaOH (carbylamine test)	Offensive smell of carbylamine	No action	No action
5. Action of acyl halides	They form mono- and also diacetyl derivatives.	Form monoacetyl derivatives only.	No action

9.4.7. Uses

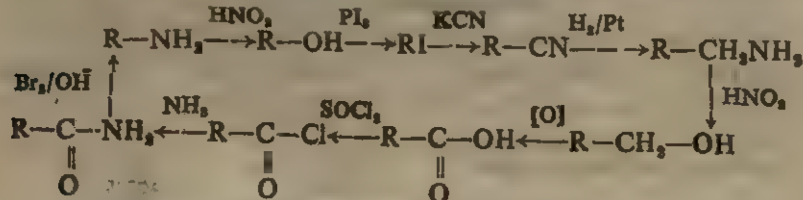
Aliphatic amines are used in the manufacture of a wide variety of products like drugs, fibres, dyes and insecticides.

Aromatic amines like aniline are widely used in the manufacture of polymers, dyes, drugs *etc.* It is also used as antioxidant and vulcanisation accelerators for the rubber industry. It is also used in sulpha drugs. The diazonium salts, obtainable from primary aromatic amines, can be converted to a variety of products (Fig. 9.4).

Low molecular mass aliphatic amines find use as solvents, intermediates in drug manufacture and reagents in organic synthesis. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents. A typical example is *n*-hexadecyltrimethyl ammonium chloride.

Stepping up and down of amine series

This may be achieved with the help of the following outline scheme :



SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

9.1. Choose the correct answer of the four alternatives given for the following questions :

(*i*) Ethylamine in alcoholic alkali with chloroform gives

(*a*) C_2H_5CN (*b*) CH_3CN (*c*) C_2H_5NC (*d*) CH_3NC

(*ii*) The structure of quaternary ammonium compounds is represented by

(*a*) $(C_2H_5)_3N$ (*b*) $(CH_3)_4N^+$

(*c*) $(CH_3)_2NH$ (*d*) CH_3NH_2.

(*iii*) Nitrating mixture is a mixture of

(*a*) Conc. HNO_3+conc. HCl (*b*) Conc. HNO_3+conc. H_2SO_4

(*c*) $NaNO_2$+conc. HCl (*d*) $NaNO_2$+conc. H_2SO_4.

(*iv*) The first product of nitration of nitrobenzene is

(*a*) TNT (*b*) Picric acid

(*c*) *o*-Dinitrobenzene (*d*) *m*-Dinitrobenzene.

(*v*) Reaction of a primary aromatic amine with nitrous acid in the cold leads to the formation of

(*a*) An alcohol (*b*) A nitro-compound

(*c*) A diazonium salt (*d*) An ether.

(*vi*) Primary amines are obtained by the hydrolysis of a

(*a*) Primary alkyl isocyanide. (*b*) Primary amine

(*c*) Quaternary salt (*d*) Primary nitro-compound

(*vii*) The major product of action of heat on butyl ethyl methyl propyl ammonium iodide is,

(*a*) Butylene (*b*) Propylene

(*c*) Ethylene (*d*) Ethanol.

(*viii*) An example of a tertiary amine is

(*a*) $C_2H_5NH_2$ (*b*) $(CH_3)_3N$

(*c*) $(CH_3)_2NH$ (*d*) $(CH_3)_4N^+Cl^-$.

(*ix*) Nitroglycerine is an

(*a*) Ether (*b*) Ester

(*c*) Acid (*d*) Aldehyde

(*x*) Which of the following is produced by the reduction of R—C≡N in the presence of sodium and ethanol.

(*a*) $RCONH_2$ (*b*) $RCOO^-NH_4^+$ (*c*) RCH_2NH_2

(*d*) $(RCH_2)_3N$

9.2. Fill in the blanks :

(*i*) The functional group in primary amines is called a.........group.

(*ii*) The functional group in secondary amines is called a.........group.

(*iii*) In hypobromite reaction the carbon is lost as.........

(*iv*) Amines are the derivatives of.........

(*v*) Lower amines are.........in water.

(*vi*) Chemically amines are.........in reaction.

(*vii*) Dissolution of long chain amines is achieved by conversion to.........

(*viii*) Nitrobenzene is prepared by treatment of.........with..........in the laboratory.

(*ix*) Nitroalkanes have.........boiling points.

(*x*) Nitroalkane on hydrolysis with acid gives.........and.........

9.3. Mark the true (T) and false (F) statement out of the following :

(*i*) Tertiary amines undergo acylation.

(*ii*) Aniline is first converted into benzoyl derivative before nitration.

(iii) AgCl dissolves in methylamine solution.
(iv) $Fe(OH)_3$ is obtained when methylamine in water reacts with $FeCl_3$.
(v) Amides are neutral since the electron pair of nitrogen is unavailable due to resonance.
(vi) Alkyl halides give pure amines on ammonolysis.
(vii) Aromatic nitro compounds are soluble in water while nitroalkanes are insoluble.
(viii) Nitration of nitrobenzene produces o-dinitrobenzene.
(ix) Sulphanilic acid contains both a basic and an acidic group.
(x) Benzenediazonium chloride on heating with ethanol gives aniline.

SHORT ANSWER QUESTIONS

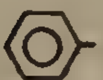
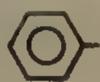
9.4. Write the IUPAC names of the following compounds :

(i) $CH_3(CH_2)_4$—$\underset{\displaystyle CH_3}{\underset{|}{C}H}CN$ (ii) *m*-$NCC_6H_4NH_2$

(iii) *p*-$CH_3OC_6H_4NO_2$ (iv) *n*-C_4H_9NC

(v) CH_3—$\underset{\displaystyle NO_2}{\underset{|}{C}H}$—$CH_2CH_2NHCH_3$ (vi) $CH_3$$\underset{\displaystyle NO_2}{\underset{|}{C}H}$—$CH_2$—$\underset{\displaystyle NO_2}{\underset{|}{C}H}CH_3$

(vii) $C_6H_5N^+(CH_3)_3Br^-$

(viii)  NH_2 (ix) $CH_3CH_2CH_2N\begin{smallmatrix} CH_3 \\ C_2H_5 \end{smallmatrix}$ (x)  CN

9.5. Draw structures, name according to the IUPAC and indicate primary, secondary and tertiary amine :
(a) eight isomeric amines of formula $C_4H_{11}N$.
(b) five isomeric amines of formula C_7H_9N that contain a benzene ring.

9.6. How will you convert :
(i) *m*-nitroaniline to *m*-iodochlorobenzene
(ii) Benzene to *m*-bromophenol
(iii) Aniline to benzoic acid
(iv) *p*-chloroaniline to *p*-chlorobenzylamine
(v) *n*-Hexanitrile to 1-aminopentane

9.7. Comment on the following :
(i) It is difficult to prepare pure amines by ammonolysis of alkyl halides.
(ii) Amines are higher boiling compounds than hydrocarbons of corresponding molecular masses but have lower boiling points than the corresponding alcohols or carboxylic acids.
(iii) Aniline is a weaker base than cyclohexylamine.
(iv) Methylamine in water reacts with ferric chloride to precipitate ferric hydroxide.
(v) Silver chloride dissolves in methylamine solution.

TERMINAL QUESTIONS

9·1 What are functional groups ?

9·2 How are cyanides and isocyanides prepared ? What are their properties and how are they distinguished from one another ?

9·3 Write the common names and IUPAC names of the following amines and nitro-compounds :

(*i*) $(CH_3)_2CHNH_2$ (with CH_3 and CH_3 attached to $>CHNH_2$)

(*ii*) $CH_3CH_2CH_2NH_2$,

(*iii*) $CH_3-\underset{\displaystyle NO_2}{\underset{|}{CH}}-CH_3$

(*iv*) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-NH_2$

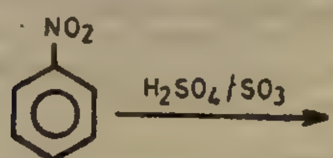
(*v*) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$

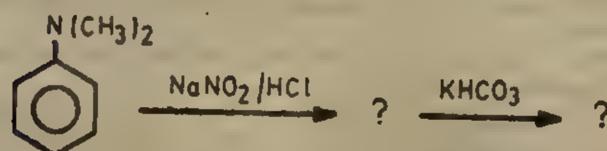
9·4 Complete the following reactions :

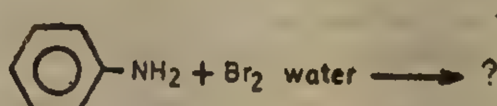
(*a*) $C_6H_5NH_2 + CH_3COCl \xrightarrow{\text{Base}}$?

(*b*) $C_6H_5NO_2 \xrightarrow[\text{NH}_4\text{Cl}]{\text{Zn}}$ ...?

(*c*) $C_6H_5NO_2 \xrightarrow{\text{Ni/H}_2}$?

(d) 

(e) 

(f) 

(*g*) $RNH_2 \xrightarrow{\text{CHCl}_3\text{/KOH}}$?

(*h*) $CH_3CH_2CH_2CONH_2 \xrightarrow[\text{Heat}]{\text{P}_2\text{O}_5}$?

$\xrightarrow{\text{H}_2\text{/Pt}}$? $\xrightarrow{\text{HNO}_2\text{/HCl}}$?

(*i*) $RI \xrightarrow{\text{NaCN}}$? $\xrightarrow{\text{H}_3\text{O}^+}$?

(*j*) $Q_2NH + HNO_2 \longrightarrow$?

9·5 (*a*) Explain the following :

(*i*) Lower amines are soluble in water.

(*ii*) Aromatic amines are less basic than ammonia while aliphatic amines are more basic.

(*b*) Which of the following is the most basic and arrange them in decreasing basic order :

(*i*) NH_3, (*ii*) $C_2H_5NH_2$, (*iii*) $C_6H_5NH_2$.

(*c*) What are nitro-compounds ? Give the general formulae of nitroalkanes and aromatic nitro-compounds.

9·6 (*a*) Give the various methods for the preparation of nitro-compounds.

(*b*) Give a brief account of the physical properties of nitro-compounds.

9·7 Discuss some of the important reactions of nitro-compounds. Mention some uses of these compounds.

9·8 (*a*) Give the nature of the reactions of nitroalkanes with

(*i*) alkalis, and (*ii*) nitrous acid.

(*b*) Give the structures for the tautomeric forms of nitroalkanes.

9·9 (*a*) What are amines ? What is the basis of their classification ?

(*b*) How is nitrous acid used to distinguish between primary, secondary and tertiary amines ?

9·10 Outline the processes employed for the manufacture of

(*i*) ethylamine, and (*ii*) aniline.

9·11 How do aliphatic primary amine and aniline react with nitrous acid ?

9·12 Explain in brief the significance of the following :

(*i*) Gabriel's synthesis

(*ii*) Hofmann bromamide reaction.

9·13 What is diazotization ? Compare the stability of alkyl and aryl diazonium salts.

9·14 Show how ethylamine could be prepared from each of the following :

(*i*) *n*-Ethylbromide

(*ii*) *n*-Ethylalcohol

(*iii*) 1-Nitroethane

(*iv*) Ethanonitrile.

9·15 (*a*) How and why is the amino group protected before nitration ?

(*b*) How and where does the $-NH_2$ group activate the aromatic ring in aniline ?

9·16 Describe the processes of halogenation, sulphonation and nitration of aniline.

9·17 (*a*) Give a laboratory test for the identification of a water insoluble compound as an amine ?

(*b*) What is Hinsberg's reagent ? How does it react with different types of amines ?

9·18 Starting from aniline how are the following obtained :

(*i*) Acetanilide,

(*ii*) Benzanilide,

(*iii*) *p*-Benzoquinone, and

(*iv*) 2, 4, 6-Tribromoaniline.

9.19 Outline the prepartion, starting from benzene, of

(*a*) nitrobenzene (*b*) phenylamine, and

(*c*) a named azo compound.

9·20 Compare and contast the reactions of phenol and phenylamine.

9·21 (*a*) Suggest a method for the preparation of methyl orange.

(*b*) How does the strength of phenylamine, as a base, compare to that of ethylamine. Give a reason for your answer.

9·22 Comment on the importance of amines as intermediates in the synthesis of other organic compounds. Explain why aliphatic amines are less important as intermediates than aromatic amines.

9·23 How will you convert nitrobenzene into :

(*a*) aniline, (*b*) phenol,

(*c*) chlorobenzene, and (*d*) an azodye.

9·24 (*a*) Describe how you could prepare a solution of benzene diazonium chloride.

(*b*) How does benzene not react with benzene diazonium chloride ?

(*c*) Under what conditions will a phenol react with a diazonium salt? What is the electrophile in this reaction ?

9 25 Write short notes on the following :

(*a*) Ambident nucleophile

(*b*) Sandmeyer reaction

(*c*) Coupling reaction

(*d*) Zwitter ion.

ANSWERS TO SELF ASSESSMENT QUESTIONS

9·1 (*i*) *c* (*ii*) *b* (*iii*) *b* (*iv*) *d*

(*v*) *a* (*vi*) *a* (*vii*) *c* (*viii*) *b*

(*ix*) *b* (*x*) *c*

9·2 (*i*) amino (*ii*) imino (*iii*) sodium/potassium carbonate

(*iv*) ammonia (*v*) soluble (*vi*) basic (*vii*) salt

(*viii*) benzene, nitrating mixture (*ix*) high

(*x*) hydroxylamine salt ; carboxylic acid.

9·3 (*i*) F (*ii*) T (*iii*) T (*iv*) T

(*v*) T (*vi*) F (*vii*) F (*viii*) F

(*ix*) T (*x*) F

9·4 (*i*) 2-Methylcyanoheptane

(*ii*) m-Cyeno aniline

(*iii*) p-ethoxynitrobenzene

(*iv*) *n*-butane isonitrile

(*v*) 3-Nitro N-methylaminobutane

(*vi*) 2, 4-dinitropentane

(*vii*) N, N, N-trimethyl N-bromoaniline

(*viii*) Aniline

(*ix*) N-ethyl N-methylaminopropane

(*x*) Benzonitrile.

9·5 (*a*) Eight isomeric amines of formula $C_4H_{11}N$

(*i*) $\overset{4}{C}H_3\overset{3}{C}H_2.\overset{2}{C}H_2.\overset{1}{C}H_2.NH_2$
1-Aminobutane
(primary)

(*i*) $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{\underset{}{C}}H(NH_2)\overset{1}{C}H_3$
2-Aminobutane
(primary)

(*iii*) $\overset{3}{C}H_3.\overset{2}{C}H(CH_3).\overset{1}{C}H_2.NH_2$
1-Amino- 2-methyl
(primary)

(*iv*) $\overset{1}{C}H_3-\overset{2}{C}(CH_3)(\overset{3}{C}H_3)-NH_2$
2-Amino 2-methylpropane
(primary)

(*v*) $\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-NH-CH_3$
N-Methyl 1-aminopropane
(secondary)

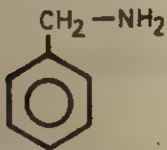
(*vi*) $CH_3-CH(CH_3)-NH-CH_3$
N-Methyl 2-aminopropane
(secondary)

(*vii*) $CH_3-CH_2-NH-C_2H_5$
N-Ethylaminoethane
(secondary)

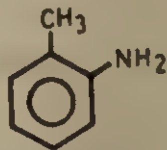
(*viii*) $CH_3-CH_2-N(CH_3)-CH_3$
N-N-dimethylaminoethane
(tertiary)

(*b*) Five isomeric amines of formula C_7H_9N

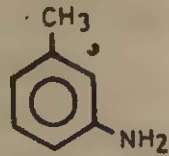
(ii)



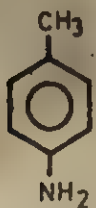
Benzylamine
(Primary)
(Phenylamino-
methane)



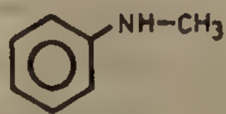
o-Aminotoluene
o-Toluidine
(Primary)
(2-Methylaniline)



m-Aminotoluene
m-Toluidine
(Primary)
(3-Methylaniline)

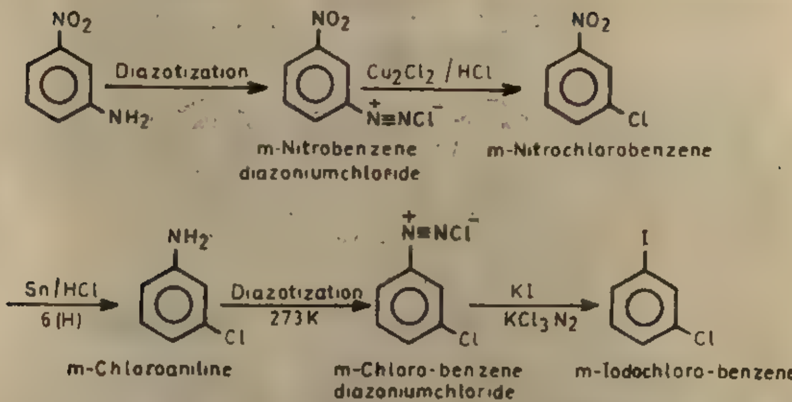


p-Aminotoluene
(p-Toluidine)
(Primary)
(4-Methylaniline)

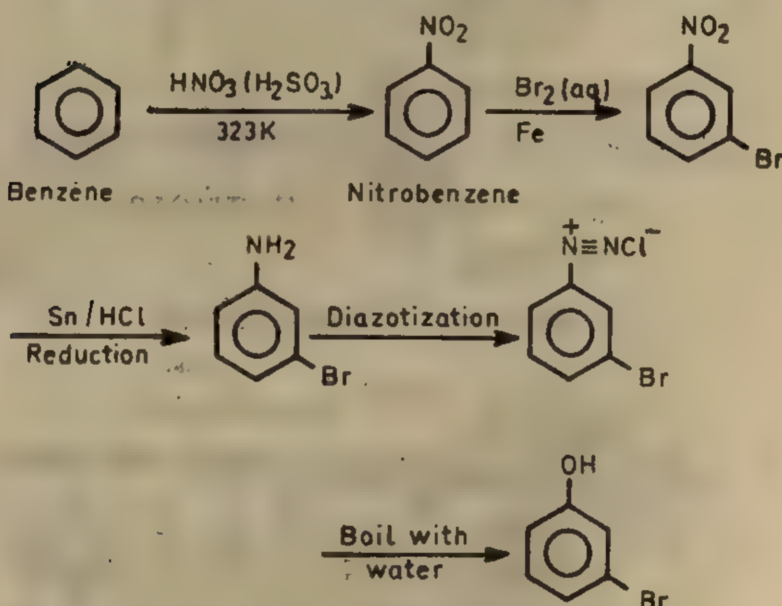


N-Methylaniline
(Secondary)
Methylphenylamine
N-Methylaminobenzene

(*i*) ***m*-Nitroaniline to *m*-iodochlorobenzene**



(*ii*) **Benzene to *m*-bromophenol**

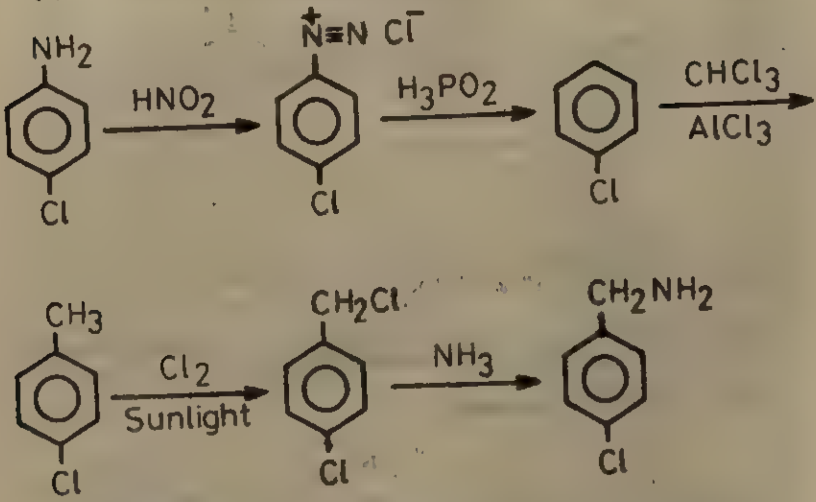


(*iii*) **Aniline to benzoic acid**

$$C_6H_5NH_2 \xrightarrow[\text{Diazotization}]{NaNO_2+HCl} \underset{\substack{\text{Benzene}\\ \text{diazonium}\\ \text{chloride}}}{C_6H_5N_2Cl} \xrightarrow[\text{Sandmeyer's reaction}]{HCN+Cu_2(CN)_2} C_6H_5CN$$

$$\xrightarrow{2H_2O} C_6H_5COOH$$

(*iv*) *p*-Chloroaniline to *p*-chlorobenzylamine



(*v*) *n*-Hexanitrile to 1-aminopentane

$$CH_3CH_2CH_2CH_2CH_2C\equiv N \xrightarrow[Zn+HCl]{4(H)} CH_3CH_2CH_2CH_2CH_2CH_2{-}NH_2$$

$$\downarrow HNO_2$$

$$CH_3(CH_2)_4CHO \xleftarrow[H_2SO_4]{K_2Cr_2O_7} CH_3(CH_2)_4CH_2OH$$

$$[O] \downarrow K_2Cr_2O_7 + H_2SO_4$$

$$CH_3(CH_2)_4COOH \xrightarrow{NH_3} CD_3(CH_2)_4COONH_4$$

$$\downarrow Heat$$

$$CH_3(CH_2)_4NH_2 \xleftarrow{NaOBr} CH_3(CH_2)_4CONH_2$$

1-Aminopentane

9·7 (*i*) Ammonolysis of alkylhalides gives a mixture of all three classes of amines along with some quaternary ammonium salt

$$NH_3 \xrightarrow{RX} \underset{\text{Primary amine}}{R{-}NH_2} \xrightarrow{RX} \underset{\text{Secondary amine}}{R_2NH} \xrightarrow{RX} \underset{\text{Tertiary amine}}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4N^+H^-}$$

Their separation is difficult. Hence, it is not easy to prepare amines by ammonolysis of alkyl halides.

(*ii*) Both primary and secondary amines are polar in nature (except tertiary amines). Therefore, molecules of amines associate due to intermolecular hydrogen bonding.

```
   CH3         CH3        CH3
   |           |          |
H...N—H.......N—H.....N—H...
   |           |          |
   H           H          H
```

Hydrocarbon molecules being non-polar boil at low temperatures. Hence amines are higher boiling compounds than hydrocarbons of corresponding molecular masses.

Due to lower electronegativity of nitrogen (present in amines) than oxygen (present in alcohols and acids) the hydrogen bonding in alcohols and carboxylic acids is stronger than in amines. Therefore, the boiling points of amines are lower than the corresponding alcohols or carboxylic acids.

(*iii*) The cyclohexyl group due to its +I inductive effect increases the availability of electrons on the nitrogen atom. This makes the amines more basic than aniline in which aromatic ring attracts electrons from the nitrogen and greatly reduces its basic character.

(*iv*) Methylamine in water provides OH^- ions which precipitate ferric hydroxide.

$$CH_3NH_2+H_2O \leftrightharpoons CH_3NH_3OH \leftrightharpoons [CH_3NH_3]^+ + OH^-$$

$$Fe^{3+}+3OH^- \longrightarrow Fe(OH)_3$$

(*v*) Methyl amine forms a soluble complex salt with silver chloride.

$$AgCl + 2CH_3NH_2 \longrightarrow \underset{\text{(Soluble complex)}}{[Ag(CH_3NH_2)_2]^+Cl^-}$$

□ □

UNIT 10

Chemistry of Representative Elements

(s and p Block Elements)

We know nothing of the true elements belonging to Nature; but as far as we can reason from the relations of the properties of matter, hydrogene is the substance which approaches nearest to what the elements may be supposed to be. It has energetic powers of combination, its parts are highly repulsive to each other, and attractive of the particles of other matter; it enters into combination in a quantity very much smaller than any other substance, and in this respect it is approached by no known body.

SIR HUMPHRY DAVY
(1812)

UNIT PREVIEW

10.1 Introduction
10.2 Hydrogen
10.3 Group 1 elements : The alkali metals
10.4 Group 2 elements : The alkaline earth metals
10.5 Group 13 elements : The boron family
10.6 Group 14 elements : The carbon family
10.7 Group 15 elements : The nitrogen family
10.8 Group 16 elements : The chalcogens
10.9 Group 17 elements : The halogens
10.10 Group 18 elements : The noble gases
Self assessment questions
Terminal questions
Answer to self-assessment questions.

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Locate on the periodic table the representative element groups and describe some properties characteristic of each group.
2. Give the characteristics of the electron configuration of the four general categories of elements.
3. Give the general periodic trends in the physical and chemical properties of the various periodic groups listed under unit preview.
4. Compare the variation in properties seen among the elements of the same periodic group.

5. Describe the general degree of reactivity of the elements of each periodic group and the behaviour of their common compounds.
6. Justify the statement, "the first element in a group is always different from the other members of the group" by taking the examples of carbon and silicon; nitrogen and phosphorus, *etc.*
7. State the possible oxidation states for each of these families of elements and the general conditions under which they are likely to form.
8. List the important compounds of each group and give their important properties.
9. Comment on the variation in properties seen among the compounds of these groups.

10.1. INTRODUCTION

Elements show periodicity in their physical and chemical properties. As we know, all the elements have been divided into four blocks, *i.e.*, s, p, d and f-blocks on the basis of electronic structure of elements. Elements belonging to the s and p-blocks (Fig. 10.1) in the periodic table are called **representative group of elements** or the **main group elements.**

The s-block elements consist of six alkali metals of group 1 and the six alkaline earth metals of group 2. The last member of each group francium (Fr) and radium (Ra) are radioactive. The valence shell electronic configurations are (ns^1) and (ns^2) for the group 1 and 2 elements respectively. A number of the properties of elements and their ions show regular trends with increasing atomic number as suggested through Fig. 10.2. Data relating to these properties are listed in Tables 10.1 and 10.2. These elements are the most electropositive elements in the periodic table. Hydrogen is also one of the members of s-block elements.

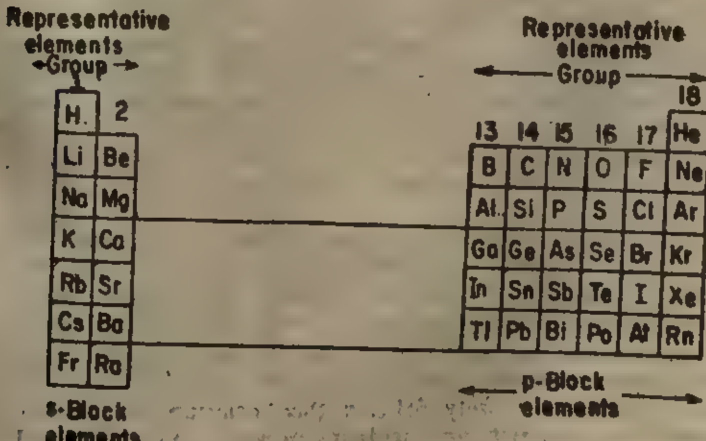


Fig. 10.1. s *and* p-*block elements of the periodic table*

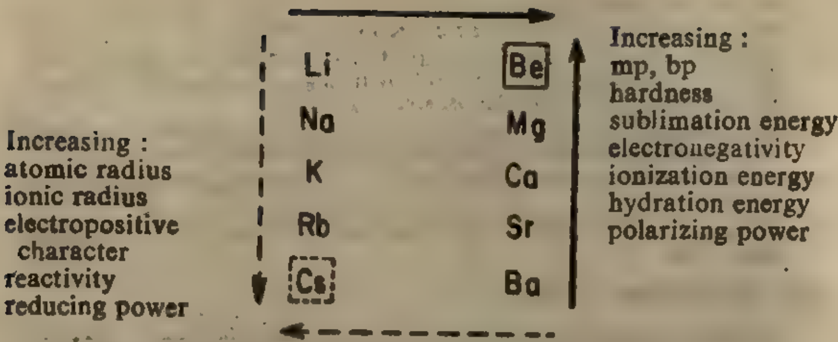


Fig. 10.2. Trends in some properties of the s-block elements.

We have seen already that s-block elements, especially the alkali metals, are very reactive. Reactivity generally increases as we move down the group. They readily form ionic compounds in combination with most non-metals except for those of the very small highly polarizing ions Be^{2+} and Li^{+} which tend to form covalent compounds. In all these compounds, all s-block elements show only one stable oxidation state which is numerically equal to the group number.

Because of the reactive nature s-block elements are found in combined forms as chlorides (Na, Mg, *etc.*), sulphates (Ca, Sr, Ba, Mg) and as silicates (Li, Be, Mg). All are prepared by the electrolysis of fused salts.

The location of the p-block elements in the periodic table is shown in Fig. 10·1.

Most of the non-metals constitute p-block elements. The valence shell electron configuration is $ns^2\,np^x$ where x varies from 1 to 6 and n from 2 to 6 There are thirty one p-block elements, a few of them are radioactive. They have their own characteristic properties and show chemical diversity in their chemical reactions. They include both inert non-metals, *e.g.*, He, Ne, Ar, Kr, Xe and extremely reactive non-metals like F, Cl, Br and I. In between these two extremes, we have non-metals of intermediate reactivities, *e.g.*, N, P, O and S.

Despite the wide range of elements involved, it is possible to make a number of useful generalizations concerning trends in the properties of the p-block elements. Some of the observed trends in the properties of the p-block elements are portrayed in Fig. 10.3.

The trends in size (covalent radius) follow the normal increase down and decrease across the table, and the variation of the first ionization potential closely follows the variation in atomic size. The trends in reactivity and oxidizing power is in conformity with the change in electronegativity ; fluorine is the most reactive element of all and has the strongest oxidizing power.

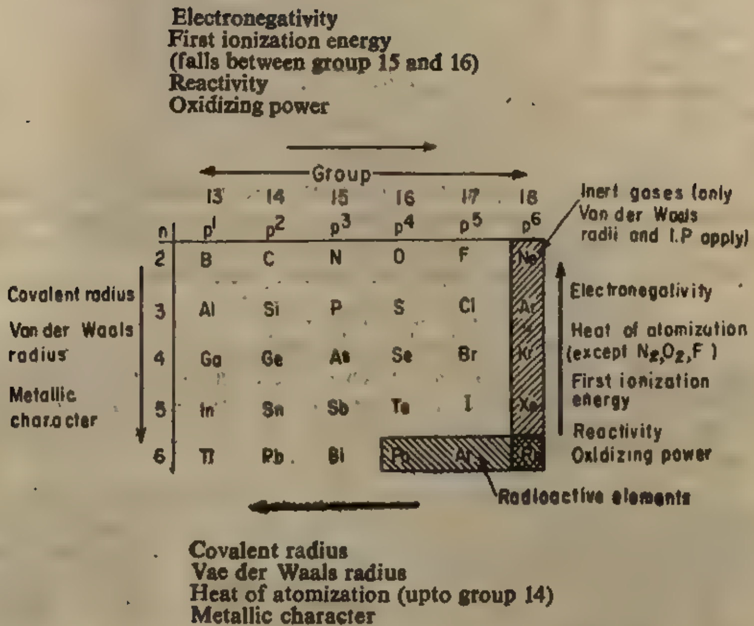
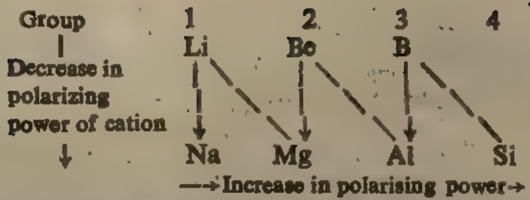


Fig. 10.3. Trends in some properties of p-*block elements*

Some data relating the trends in the properties of the elements are given in Tables 10.4, 10.6, 10.9, 10.14, 10.18 and 10.24. As compared to s-block elements p-block elements show : more dissimilar chemistries ; less regular changes in properties as a group is descended, and more than one stable oxidation state (the highest oxidation state being, Group number —10). The highest oxidation state becomes less stable as we move from group 13 to 17, parallelling an increase in the energy differences between the s- and the p-orbitals of the valence shell. Within a group, the higher oxidation state becomes progressively less stable with respect to the lower oxidation state as the atomic number increases. This trend is commonly referred to as **inert pair effect.**

The first member of each group differs in many ways from the heavier members of the group. These differences arise due to the difference in **size and electronegativity** between the first and second members of the groups being much greater than that between any other successive group elements. The unavailability of d orbitals for bonding among the first row elements (Li to F) is also responsible for the anomalous behaviour of the first member of each group. The first element of a group often shows resemblances to the second element of the neighbouring group on the right. This type of behaviour is known as **Diagonal Relationship.**



This similarity is observed to some extent between lithium and magnesium and even more closely between beryllium and aluminium, as well as between the non-metals boron and silicon. The similarity in behaviour is attributed largely to similar ionic sizes,

$$(Li^+ r/pm=76\ ;\ Mg^{2+} r/pm=72).$$

The main structural trend for the elements (particularly elements across the first and second short periods) and representative compounds is from ionic solids early in the periods, through covalent and often polymeric solids around group 14 to liquid and gaseous covalent compounds later in the periods.

The valence orbitals of the first and second short periods elements, 2s and 2p, can hold at most a total of four electron pairs in their compounds. Li, Be and B have less number of electrons than the maximum possible number. Such compounds as $BeCl_2$ and BF_3 are called **electron deficient** compounds. They tend to achieve electronic saturation in a variety of ways, *viz.*

(*i*) Polymerization, *e.g.*, $BeCl_2$ is a chain polymer in the solid state.

(*ii*) Multiple bonding, *e.g.*, BF_3, in which a lone pair of electrons of each fluorine atom may be used in a $B \leftarrow F$ dative π-bond involing the vacant orbital on the boron atom.

(*iii*) Formation of complexes in which electrons are received from a donor molecule, *e.g.*, $F_3B \leftarrow NH_3$. Boron compounds, thus, behave as Lewis acids.

(*iv*) Loss of all valence electrons to form a cation *e.g.*, Na^+ and Mg^{2+}.

A characteristic feature of the first row elements, carbon, nitrogen and oxygen, is their ability to form π-multiple bonds. This type of bonding is not particularly strong for the second and subsequent rows of elements. However, these heavier p-block elements form π-bonds with lighter elements (O and N) through their outer d orbitals ($d\pi$-$p\pi$ bonding). We shall discuss this point later in this unit.

The elements and their compounds play a vital role in chemistry and in our lives. Hydrogen and oxygen react with each other to form H_2O (water), a simple molecule, whose unusual properties are necessary for the development and maintenance of life.

Sugar (or carbohydrates), an important source of energy contains C, H and O. Proteins, the body-building materials contain

C, H, O and N as their constituents. Detergents, vitamins, fertilizers, medicines, *etc.* all contain some of these elements. Some of the inorganic chemicals such as sodium hydroxide and mineral acids (H_2SO_4, HCl, HNO_3), produced on a large scale, contain these elements. Caustic soda (NaOH) and sulphuric acid are prime industrial chemicals. Their production and pattern of consumption is an index of a nation's industrial strength.

10.2. HYDROGEN

Hydrogen occupies a unique position in the periodic table. Hydrogen, being the first element has the simplest atomic structure amongst all the elements. It has a nucleus with single positive charge and one electron in the orbit.

In its properties, it behaves like alkali metals (group 1) as well as like halogens (group 17). Hydrogen, thus, finds its assignment both with alkali metals and halogens. It can lose its only electron to form H^+ ion, and thus it resembles alkali metals (M) which yield M^+ ions. It can also form H^- ion by gaining one electron similar to halogens (X) forming X^- ions. In its atomicity, it also resembles halogens (both halogens and hydrogen exist in diatomic form).

Hydrogen can also form a single covalent bond with other atoms like C, Si, *etc.* Therefore, hydrogen can be considered as non-metal in respect of some of its properties. Although hydrogen shows similarities in its chemical properties to both alkali and halogens, it differs in many ways.

Hydrogen resembles the alkali metals in its ability to form hydrated positive ion.*

It is believed that hydrogen is the most abundant element in the universe. On earth all hydrogen is combined, much of it with oxygen as water. Hydrogen exists uncombined as a diatomic molecule. It occurs naturally as a mixture of three isotopes, protium $\left[\,^1_1H\,\right]$, deuterium $\left[\,^2_1H\,\right]$ or ^2_1D tritium $\left[\,^3_1H\,\right]$ or ^3_1T.

Hydrogen is the only element whose isotopes have special names and symbols. Tritium is radioactive and hence undergoes nuclear decay.

$$^3_1H \longrightarrow \,^3_2He + \beta$$

*The bare proton being very small ($\sim 1.5 \times 10^{-3}$ pm compared with the usual atomic and ionic sizes of 50—220 pm) never exists in the free state in condensed phase. It gets combined with other molecules usually with those of the solvent. Thus hydrogen can form the hydrogen ion only when its compounds are dissolved in a solvent that can solvate protons.

$$HCl + H_2O \longrightarrow [H_3O]^+ + Cl^-$$

Compounds that form solvated hydrogen ions in polar solvents are called **protonic acids.**

Hydrogen

^1_1H mass no. 1
Hydrogen or protium
Abundance 99·984 %

Deuterium

^2_1H or ^2_1D mass no. 2
Heavy hydrogen
Abundance 0·16 %

Tritium

^3_1H or ^3_1T mass no. 3
Tritium
Abundance 10^{-15} %

Isotopes of hydrogen

Tritium is belived to be formed in the upper atmosphere as a result of cosmic ray activity. Since the electronic configuration of isotopes is identical, the chemical properties are similar, but owing to their different masses, they have different physical properties. Deuterium and tritium, being heavier, can be used as 'tracers' in many studies because when hydrogen is replaced by them, the reaction rates will be lower and they can be detected. The largest differences between compounds of ^2_1D and ^1_1H are observed in water (H_2O) and heavy water (D_2O).

The preparation of hydrogen gas is usually a reduction from the +1 state. The reduction is achieved either electrolytically or chemically. Electrolytic hydrogen is the purest commercial form and is produced by the electrolysis of acidulated water. Water can be chemically reduced by means of a number of reducing agents, *e.g.* Na and Ca metals.

$$2Na(s)+2H_2O \longrightarrow H_2(g)+2Na^++2OH^-$$

If the pH of water is lowered below 7·0, the rate of reduction by a metal increases. Zinc, for example, reacts readily with dilute HCl or H_2SO_4.

$$Zn(s)+HCl\ (aq) \longrightarrow ZnCl_2(aq)+H_2(g)$$

Metals, such as zinc or aluminium can also produce hydrogen from basic solutions, as well

$$Zn(s)+2OH^-+2H_2O \longrightarrow H_2(g)+[Zn(OH)_4]^{2-}$$

$$2Al(s)+2OH^-+6H_2O \longrightarrow 3H_2(g)+2[Al(OH)_4]^-$$

Oxidation state +1 : In most of its compounds, hydrogen is covalently bonded to a more electronegative atom, *e.g.*, HF, HCl, HBr, HI, H_2O, H_2S, NH_3, B_2H_6, CH_4, *etc.* Each of these can be produced by direct combination of the elements.

Other compounds showing +1 oxidation state, *e.g.*, HOCl, H_2SO_4, $NaHCO_3$, NaOH, *etc.* are very common.

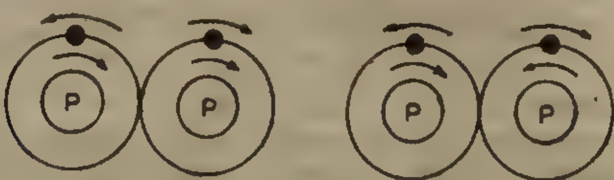
Oxidation state −1 : Since the acquisition of an electron by hydrogen to form H^- ions requires energy (−72.8 kJ mol^{-1}), it can be formed only with those elements which have low ionization energies such as the alkali and the alkaline earth metals. Compounds in which hydrogen is bonded to a more electropositive element are known as hydrides. Various types of hydrides are possible.

Ionic hydrides : hydrides of groups 1 and 2 metals.

Covalent hydrides : hydrides of groups 13, 14 and 15 elements.

Metallic hydrides : hydrides of transition elements.

Molecular hydrogen also possess two isomers of different internal energy which arise because of the direction of spins of the two nuclei. If the spins are parallel, the isomer formed is called ortho dihydrogen while it is called para dihydrogen if the spins are opposite.



Para spins (Ortho dihydrogen) Opposite spins (Para dihydrogen)

10.3. GROUP 1 ELEMENTS : THE ALKALI METALS

The elements of group 1 are called alkali metals. The word alkali is derived from an ancient Arabic word meaning "plant ashes"; both radium and potassium are found in the ashes of burned plant material.

With their ns^1 electron configuration, they are the most reactive of the metals. The elements and their compounds are chemically very similar, owing to their similar valence shell electron configuration. Difference that exist primarily reflect the variation in atomic radius. All the metals in the group have body centered cubic structures at room temperature. Hence, the metals are soft and have low densities, melting and boiling points. The relatively low melting and boiling points, densities, *etc.* are consequences of the fairly weak bonding forces, since each atom can furnish only one electron for metallic bonding. Because their outer electrons are loosely held, the metals are good electrical and thermal conductors. Their

reactivity, within the family, generally increases with increasing atomic number as ionization energy decreases. Because of low ionization energies, the metals are strong reducing agents and can reduce almost any electronegative element like N, P and S.

Alkali metals, in their compounds, exhibit the +1 oxidation state. Their compounds are generally ionic.

It is easy to excite the valence electrons of these metals to higher energy states. When the excited electrons return to the ground state, there is emission of radiation in the visible region. Now when one of their salts is introduced in the Bunsen burner flame, lithium salts impart a beautiful red colour to the flame, sodium salts give a brilliant yellow colour, whereas potassium salts produce a violet coloured flame. These colours are intense enough to serve as useful qualitative tests called flame tests for the detection of these metals. On irradiation with light, the elements emit electrons and thus potassium and caesium find use in photoelectric cells. These elements, because of their reactive nature, are always found combined with other elements. Some of the important general properties of the group 1 elements are given in Table 10.1.

TABLE 10.1 : Properties of group 1 elements

Property	*Li*	*Na*	*K*	*Rb*	*Cs*
Atomic number	3	11	19	37	55
Electron structure	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$
Abundance in earth's crust (ppm)	65	28300	25900	310	7
Atomic (Metallic) radius [a] (r/pm)	155	190	235	248	265
Ionic radius[b], r_{M^+}/pm	76	102	138	148	169
Melting point, T/K	453	370.8	336.8	312	301.5
Boiling point, T/K	1590	1155.9	1039	961	963
Ionization energy, IE/kJ mol^{-1}	520	495	418	403	374
Electronegativity[c]	1.15	1.0	0.9	0.9	0.85
Electron affinity/ kJ mol^{-1}	−57	−21	—	—	—
Density at 293 K, ρ/g cm^{-3}	0.53	0.97	0.86	1.53	1.87
Reduction potential at 298 K E°/K $M^+(aq)+e^- \rightarrow M(s)$	−3.04	−2.71	−2.93	−2.99	−3.02

a=Metallic radius (coordination number=8); b=ionic radius when coordination number is 6; c=at Pauling scale.

10.3.1. Chemical Properties of Alkali Metals and their Trends

The ionization energies reveal that the single electron in the outer shell of the group 1 is easily removed. All the reactions of these metals are characterized by the facile loss of one electron per metal atom. They are very strong reducing agents. Even such weak acids such as water (alcohol or acetylene) and ammonia react with these metals to evolve hydrogen. The reaction with water is vigorous.

$$2M(s)+2CH\equiv CH(g) \longrightarrow 2M-C\equiv CH+H_2(g)$$

$$2M(s)+2H_2O(l) \longrightarrow 2MOH(aq)+H_2(g)$$

Alkali metals dissolve in liquid ammonia to give blue solutions which upon standing slowly liberate hydrogen :

$$2M(s)+2NH_3(l) \longrightarrow \underset{\text{(Metal amide)}}{2MNH_2}+H_2(g)$$

The blue colour of metal-ammonia solutions is due to the presence of the solvated electrons.

The alkali metals react readily with most of the non-metals (H_2, O_2, S,X_2, C, P, N_2, *etc.*) forming ionic compounds.

$$2M(s)+H_2(g) \longrightarrow 2MH(s)$$

$$2M(s)+X_2(g) \longrightarrow 2MX(s)$$

The direct reactions with N_2 and O_2 are not so general, however, only Li reacts directly with oxygen forming a notmal oxide, Li_2O or with nitrogen to form a nitride, Li_3N. This behaviour of lithium is similar to magnesium which has a diagonal relationship with lithium. In the reaction with oxygen, sodium forms the peroxide.

$$2Na(s)+O_2(g) \longrightarrow Na_2O_2(g)$$

while K, Rb and Cs form superoxides.

$$M(s)+O_2(g) \longrightarrow MO_2(M=K, Rb, Cs)$$

10.3.2. Anomalous Behaviour of Lithium

As usual, the first member of the group, Lithium is much more electronegative than the other members of the group. Further lithium differs in chemical behaviour from its congeners and this is because of the significant difference in their sizes and electronegativity values. It resembles magnesium of group 2. The ions of both the metals have the same size. The following properties may be noted for lithium and magnesium which are in contrast to the properties of the other alkali metals.

(*i*) Unlike the other members of the group, lithium reacts with N_2 to form a nitride in the same way as magnesium does.

(*ii*) Both metals are harder and have a higher melting point than the other metals in their respective groups.

(*iii*) Their hydroxides are less soluble and decompose on heating to give Li_2O and MgO.

(*iv*) Both Li and Mg react slowly with cold water whereas other alkali metals react vigorously.

(*v*) Lithium hydroxide, carbonate and nitrate decompose on heating to give Li_2O. The other alkali metal hydroxides and carbonates remain unchanged on heating whereas the nitrates decompose to give nitrites.

(*vi*) LiF, Li_3PO_4 and Li_2CO_3 are much less soluble in water than the corresponding salts of the other alkali metals. The solubilities are comparable to those of the corresponding magnesium compounds.

(*vii*) Both Li and Mg (Grignard reagent) form organo compounds that are covalent. Other alkali metals do not form such compounds.

10.3.3. Compounds of the Alkali Metals

Oxides : The alkali metals combine directly with oxygen to yield monoxide, M_2O, the peroxide, M_2O_2 or (except for Li) the superoxide, MO_2. Stability of the peroxides and superoxides increases with increasing size of the alkali metal ion. Owing to lattice defects, many of the oxides are coloured; Na_2O_2, for example, is usually available as a yellow solid. The oxides react with water vigorously forming metal hydroxide.

$$M_2O(s)+H_2O(l) \longrightarrow 2MOH(aq)$$

$$M_2O_2(s)+2H_2O(l) \longrightarrow 2MOH(aq)+H_2O_2(l)$$

$$2MO_2(s)+2H_2O \longrightarrow 2MOH(aq)+H_2O_2(l)+O_2(g)$$

Hydroxides : Alkali metal oxides react with water to give hydroxides. These are the most basic of hydroxides and their basic strength increases from lithium to caesium, since the dissociation reaction

$$MOH(aq) \longrightarrow M^+(aq)+OH^-(aq)$$

occurs with great ease for the large cations.

Both NaOH and KOH are important industrial chemicals.

Sodium hydroxide is manufactured by the electrolysis of a saturated solution of sodium chloride. Its solution shows the usual properties of bases. The solid hydroxide is stable to heat ; it melts but does not decompose. Potassium hydroxide is similar to NaOH in all respects. It is, however, a stronger alkali and more soluble in alcohol and is, therefore, used in organic reactions in place of caustic soda. Its aqueous solution is known as potash lye.

Both NaOH and KOH are used in the manufacture of soap. They are used for the absorption of CO_2 and SO_2 gases. Sodium

hydroxide is used in the manufacture of paper and viscose rayon. It is used in petroleum industry for refining. It is also used in the purification of bauxite for aluminium production.

Oxyanion salts : A large range of oxyanion salts are known for the alkali metals. They are readily prepared by the addition of a metal hydroxide to the appropriate acid. The salt, Na_2CO_3, 'washing soda' is an important commercial chemical which is manufactured by Solvay process, It involves the reaction of CO_2 with ammoniated brine solution, when sodium bicarbonate is formed; which crystallized out on being sparingly soluble in water. Sodium bicarbonate is calcined to get sodium carbonate.

$$NH_3+H_2O+CO_2 \longrightarrow NH_4HCO_3\,(aq)$$

$$NH_4HCO_3+NaCl \longrightarrow NaHCO_3\,(s)+NH_4Cl$$

$$2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3+CO_2+H_2O$$

Potassium carbonate is produced by treating KCl (or carnallite) with H_2SO_4 and, in turn, by heating with limestone and coal. The black ash is obtained which is lixivated to get K_2CO_3.

$$KCl+H_2SO_4 \longrightarrow KHSO_4+HCl$$

$$KHSO_4+KCl \longrightarrow K_2SO_4+HCl$$

$$K_2SO_4+2C+CaCO_3 \longrightarrow K_2SO_3+CaC+2CO_2$$

It can also be produced by passing CO_2 through a solution of KOH, when the bicarbonate obtained is calcined to get the salt.

$$KOH+CO_2 \longrightarrow KHCO_3$$

$$2KHCO_3 \longrightarrow K_2CO_3+CO_2+H_2O$$

Sodium carbonate is used (*i*) in the manufacture of glass, caustic soda, soap powder, (*ii*) in the softening of water, and (*iii*) in industry as washing soda. Potassium carbonate is more expensive than sodium carbonate. It is used (*i*) in the manufacture of soft soap, hard glass, caustic potash and other potassium salts, (*ii*) in in washing wool, (*iii*) as a drying agent, and (*iv*) as a constituent of fusion mixture.

Anhydrous sodium sulphate is obtained as a by-product (salt cake) in the manufacture of HCl.

$$2NaCl+H_2SO_4 \longrightarrow Na_2SO_4+2HCl$$

Its hydrated salt, $Na_2SO_4\,10H_2O$ is known as Glauber's salt. It finds use (*i*) in the manufacture of craft paper, (*ii*) in textile industry, and (*iii*) in medicine as a purgative.

Potassium sulphate is produced from the naturally occurring minerals, *e g.*, schonite, $K_2SO_4.MgSO_4.6H_2O$ by treating with KCl.

$$K_2SO_4.MgSO_4\,6H_2O+2KCl \longrightarrow 2K_2SO_4+MgCl_2+6H_2O$$

On cooling K_2SO_4 gets crystallized out from the solution as it is not very voluble in water. It forms alums, *e.g.*, potash alum. It is used (*i*) as fertilizer, (*ii*) in the manufacture of potash alum and glass.

The solubility of the oxyanion salts depends to some extents on the relative sizes of the cations and anions. If the anion is small (*e.g.* OH^-) trends in lattice energy dominate and solubilities increase down the group. If the anions are large (*e.g.*, SO_4^{2-}) the lattice energy mainly depends on the anion and generally constant for a series of metals. Hence, trends in the hydration energy dominate and solubilities increase up the group.

10.4. GROUP 2 ELEMENTS : THE ALKALINE EARTH METALS

The elements Be, Mg, Ca, Sr and Ba of group 2 are known as alkaline earth metals. The term earth had its origin from the property of any non-metallic substance (mostly oxides) which was not very soluble in water and stable at high temperatures. On the basis of alkaline behaviour of the oxides of group 2 metals, the group 2 metals were called alkaline earths.

They all have two electrons (ns^2) in the highest energy level, which are both lost in ionic compound formation, though not as easily as the valence electron of an alkali metal. Like the alkali metal compounds, nearly all group 2 metal compounds are ionic.

Those of Be exhibit a great deal of covalent character. This is because the small sized Be^{2+} (high charge density) has high polarzing power. In this respect, beryllium compounds resemble those of aluminium in group 13 (diagonal relationship).

Group 2 elements are close relatives of groups 1 elements. They are somewhat harder, with higher melting and boiling points, denser and less reactive (sodium reacts with water violently, magnesium reacts only with hot water). But their general pattern of reactivity is quite similar to that of group 1 elements. Since they each have two valence electrons, they have stronger bonding and show higher cohesive properties than their group 1 neighbours. Thus, they are harder. Except barium, all the metals in the group have close packed (more rigid) metallic structures than those of the alkali metals. Barium has body centered cubic lattice. These elements are less electropositive than alkali metals. As a group, they resemble the less electropositive metals of group 1 and the metal most resembling lithium turns out to be magnesium—the diagonal relationship. They are good conductor of heat and electricity. Trends in properties of the elements like atomic and ionic radii, density, electronegativity and ionization energy are as would be expected from their position in the periodic table (Table 10.2 ; Class XI, Unit 5).

All except magnesium impart characteristic colours to the flame, Ca-brick red, Sr-crimson and Ba-apple green. Metals are reducing

agents. Their strength as reducing reagents (measured by redox potential data) is shown by the vigour with which they reduce water and acids to hydrogen. These elements because of their reactive nature are found in combined forms as carbonates, sulphates and silicates. As usual the behaviour of beryllium and its compounds is closer to that of aluminium than it is to that of the other alkaline earth metals. This is again because of the significant difference in their sizes and electronegativity values. Their general properties and the trends observed in their properties are summarized in Table 10.2.

TABLE 10.2 : Properties of group 2 elements

Property	*Be*	*Mg*	*Ca*	*Sr*	*Ba*
Atomic number	4	12	20	38	56
Electron structure	$[He]2s^2$	$[Ne]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$
Abundance in earth's crust (ppm)	6	20900	36300	150	430
Atomic (metalic), radius *a* r/pm	112	160	197	215	222
Ionic radius b, $r_{M^{2+}}$/pm	27	72	100	118	135
Melting point, T/K	1560	922	1112	1041	1000
Boiling point, T/K	3243	1378	1767	1654	1413
Density, ρ/g cm^{-3} at 293 K	.85	1·74	1.55	2·63	3.62
Ionization energy, IE/kJ mol^{-1} 1st	899	737	590	549.2	503
Ionization energy, IE/kJ mol^{-1} 2nd	1750	1450	1115	1060	960
Electronegativity^c	1.5	1.3	1.1	1.0	0.95
Electron affinity/ kJ mol^{-1}	+100	+30	—	—	—
Reduction potential at 298K, $E°$/V $M^{2+}(aq)+2e^- \longrightarrow M(s)$	−1.85	−2.37	−2.87	−2.89	−2.91

a=Metallic radius (coordination number=12 for all elements except Ba for which coordination number is 8). *b*=Values are for coordination number 6 except for Be^{2+} for which coordination number is 4. *c*=Pauling scale.

10.4.1. Chemical Properties of Alkaline Earth Metals and their Trends

The alkaline earth metals show a wide range of chemical properties than the alkali metals. Although the group 2 metals are not quite as reactive as the group 1 metals. Just as the chemistry of alkali metals is dominated by the unipositive (M^+) oxidation state, the dipositive oxidation state (M^{2+}) is the predominant valence of group 2 elements. Under usual conditions the M^{2+} ions of group 2 metals are more stable than their M^+ counterparts because of the increased hydration energies (for ions is solution) and lattice energies (for ions in crystal) which accompany the more highly charged ions. The heat of hydration of the M^{2+} ion of group 2 metals decreases with an increase in their ionic size. Compared to the heat of hydration of alkali metal ions of comparable size, the heats of hydration of the alkaline earth ions are approximately four times greater [*e.g.*, ΔH_{hyd} Na^+ (size 102 pm)=—397 kJ mol^{-1} ; $\Delta H_{hyd} Ca^{2+}$ (size 100 pm)=—1650 kJ mol^{-1}. Thus, the alkaline earth metal ions, because of their higher charge to size ratio tend to exert a much stronger electrostatic attraction on water molecules surrounding them.

In view of the high second ionization energy of the alkaline earth metals, their strong reducing nature seem surprising. This is because the higher hydration energy of the dipositive ions compensates for this and so the reduction potentials of Ca, Sr and Ba are almost the same as those of their group 1 counterparts K, Rb and Cs.

Group 2 metals react readily with hydrogen, oxygen, sulphur, carbon, nitrogen and halogens forming MH_2, MO, MS, MC_2, M_3N_2 and MX_2 respectively. These compounds have the properties expected for ionic compounds of these non-metals, with the exception of the beryllium compounds.

$$MO(s)+H_2O(l) \longrightarrow M(OH)_2\,(aq)$$

$$M_3N_2(s)+6H_2O(l) \longrightarrow M(OH)_2(aq)+2NH_3(g)$$

$$MC_2(s)+2H_2O(l) \longrightarrow M(OH)_2(aq)+C_2H_2(g)$$

At high pressures and temperatures, Ba forms the peroxide from which H_2O_2 is produced by adding acid.

$$BaO_2(s)+2H^+ \longrightarrow Ba^{2+}+H_2O_2$$

Except for Be, the alkaline earth metals react with water to form H_2 gas.

$$M(s)+2H_2O(g) \longrightarrow M^{2+}(aq)+H_2(g)+2OH^-(aq)$$

The more reactive Ca, Sr and Ba react with water at room temperature, but magnesium reacts only with boiling water. Beryllium, even when red hot, is unreactive toward water. The lower reactivity of group 2 metals as compared to group 1 metals is well evident

from the above reactions. Of all the group 2 metals, beryllium alone dissolves in base with the evolution of hydrogen.

$$Be(s)+2OH^-(aq)+2H_2O(l) \longrightarrow [Be(OH)_4]^{2-}(aq)+H_2(g)$$

10.4.2. Compounds of the Alkaline Earth Metals

Oxides. The oxides of the alkaline earth metals can be prepared by burning the metals in oxygen.

$$2M(s)+O_2(g) \longrightarrow 2MO(s)$$

Thermal decomposition of the carbonates of Ca, Sr and Ba also gives the normal oxides. At high temperatures and pressures, Ba forms the peroxide, BaO_2. It is the most stable of all the group 2 peroxides. All the oxides except that of Be, hydrolyse with the formation of corresponding hydroxides which are strong bases.

The high thermal stability of the oxides is a consequence of their high lattice energies and heats of formation.

Hydroxides. The alkaline ear th metal oxides react with water to form the hydroxides $M(OH)_2$. These are weaker bases than the hydroxides of alkali metals, because of their lower solubility and reduced ionic character. The solubility of the hydroxides increases as we move down the group. Since OH^- and M^{2+} ions are comparable is size, the lattice energy of the hydroxides depends on the cation size and so decreases as we move down the group. However, increase in size down the group causes decrease in heat of hydration also and under the circumstances the lattice energy dominates giving rise to the increasing solubility of the heavier hydroxides.

The reaction of oxides with water is an exothermic process, known as slacking. Slacked lime is $Ca(OH)_2$ and is prepared from lime or quickime, CaO.

Oxyanion salts. The alkaline earth metals form a wide range of oxyanion salts, but it is significant to know that solid bicarbonates cannot be produced, presumably because of instability caused by the strong polarizing power of the M^{2+} ions.

Carbonates are found in natural forms. They are insoluble in water but soluble in dilute acids because of the formation the bicarbonate ion

$$\underset{\text{(Insoluble)}}{CaCO_3(s)}+\underset{\text{carbonic acid}}{CO_2(g)+H_2O(l)} \longrightarrow \underset{\text{(Soluble)}}{Ca(HCO_3)_2(aq)}$$

They are decomposed on heating to oxides and CO_2.

$$MgCO_3(s) \xrightarrow{\text{Heat}} MgO(s)+CO_2(g)$$

In qualitative analysis, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} can be precipitated as white insoluble carbonates from basic solutions. Alkaline earth metal bicarbonates occur only in solution.

Magnesium and calcium bicarbonates are unstable to heat and cause temporary hardness of water. Since on boiling these bicarbonates decompose to insoluble carbonates, temporary hardness of water can be removed by heating.

$$Ca(HCO_3)_2(aq) \longrightarrow CO_2(g)+H_2O+CaCO_3(s)$$

$MgCO_3$ is used as a refractory material and in certain medicinal preparations. Limestone is used in the manufacture of cement, quicklime (or lime), washing soda and glass. Marble is used for building purposes. Limestone is an extremely important raw material in many industrial reactions.

Sulphates of group 2 metals occur in nature. They can be prepared by treating the metal carbonates or hydroxides with dilute H_2SO_4. The solubility of the sulphates decreases markedly from magnesium to barium, the latter being insoluble.

Sulphates of Mg, Ca and Ba are quite important. Magnesium sulphate in the hydrated form, $MgSO_4.7H_2O$ is called Epsom salt. It is used to treat fabrics so that they readily accept dyes, to make fire proof fabrics, as a fertilizer, in soaps, paints and medicinally. It is a mild purgative. The mineral gypsum is $CaSO_4.2H_2O$ and is used to make plaster and plasterboard—a building material commonly called sheetrock. Gypsum on heating loses a molecule of water to give a semihydrate ($CaSO_4.\frac{1}{2}H_2O$) called plaster of paris which is used as a dehydrant and for making plaster casts in orthopaedic surgery. The sulphates are remarkably stable to heat. Gypsum is used in the manufacture of cement, and fertilizer also.

Barium sulphate is used as a whitener in photographic papers and a filler in papers and polymeric fibres. Medicinally it is used for X-ray diagnosis of intestinal tract disorders as $BaSO_4$ is opaque to X-rays. It is poisonous but being insoluble its suspension can be swallowed without harm.

The increase in solubilities of the sulphates, and carbonates as we move up the group is explained by the rise in hydration energy from Ba to Be being rapid than the increase in lattice energy.

Halides. The alkaline earth halides (MX_2) are formed by the direct union of the metals with halogens. Beryllium chloride is conveniently prepared from the oxide :

$$BeO+C+Cl_2 \xrightarrow{870-1070\ K} BeCl_2+CO$$

Beryllium being less metallic in nature than the other members of the group form covalent halides having low melting points. They are volatile and show no electrical conductivity in the fused anhydrous state.

The halides of alkaline earth metals with any particular halogen show an increase in ionic character from Be to Ba and the

halides of any particular metal show an increase in ionic character for a decrease in anionic radius from $I^- \longrightarrow F^-$.

The fluorides of group 2 metals have higher lattice energies than the other halides and are consequently less soluble in water. The solubility of the other halides decreases from Mg to Ba. From the solution, hydrated salts such as $MgCl_2.6H_2O$, $CaCl_2.6H_2O$ and $BaCl_2.2H_2O$ can be crystallized out where the water is associated with the cation by ion-dipole interactions.

In the solid state, the halides BeF_2, $BeCl_2$ and $BeBr_2$ are polymeric and have chain structures (Fig. 10.4) with each Be atom being tetrahedrally coordinated. The coordination number of Be drops as the compound is heated and vaporized to give Be_2Cl_4 and finally $BeCl_2$. Beryllium chloride readily hydrolyzes in water to form an acidic solution.

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$

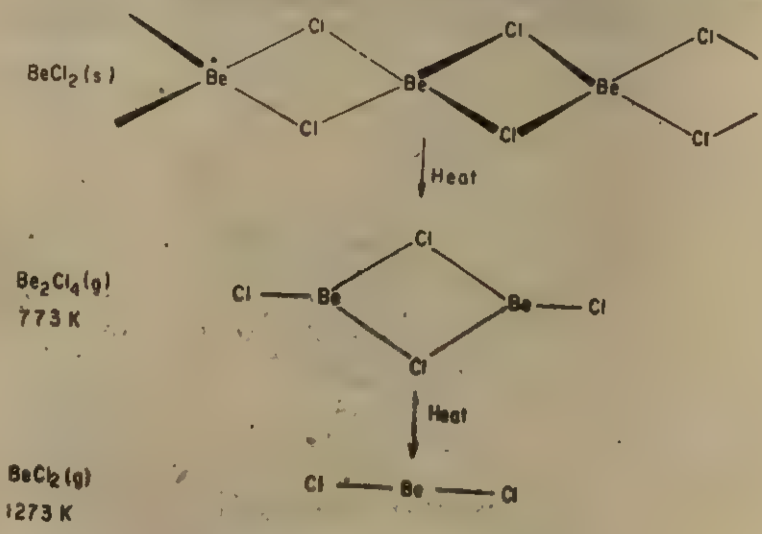
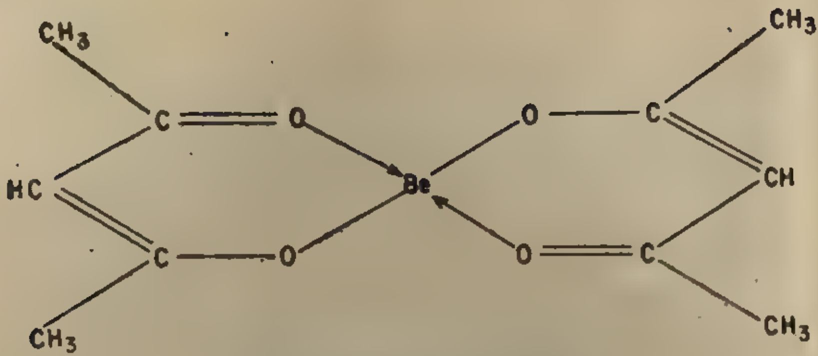


Fig. 10.4. Structure of $BeCl_2$

Complexes. As with the alkali metals, the high degree of basicity prevents any significant coordination chemistry. Alkaline earth metal ions show an increased tendency to form complex compounds compared to alkali metal ions because of their smaller size and higher charge. The tendency is the greatest for beryllium. In its complexes, it almost invariably shows the tetrahedral coordination number of four (it cannot be greater, because of the small size of Be^{2+}). Examples are $[Be(H_2O)_4]^{2+}$ in its salts, BeF_4^{2-} the vapour of $(BeCl_2)_2$ which contains bridging chlorines and Be (acetylacetone)$_2$.



Bis-acetylacetonatoberyllium (II)

Beryllium also forms complex oxyanion compounds such as $[Be_4O\ (acetate)_6]$ and $[Be_4O(NO_3)_6]$ [Fig. 10.5). Ethylenediaminetetraacetic acid (EDTA) is an important reagent which forms complexes with many metal ions, including Mg^{2+} and Ca^{2+}. The ligand wraps itself around the metal in the manner as shown in Fig. 10·6.

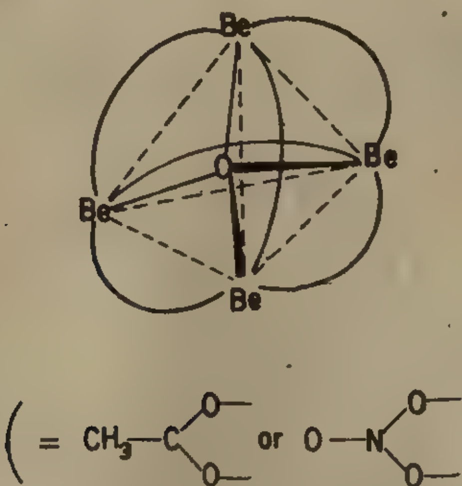


Fig. 10.5. Shape of $[Be_4O\ (acetate)_6]$ and $[Be_4O\ (NO_3)_6]$.

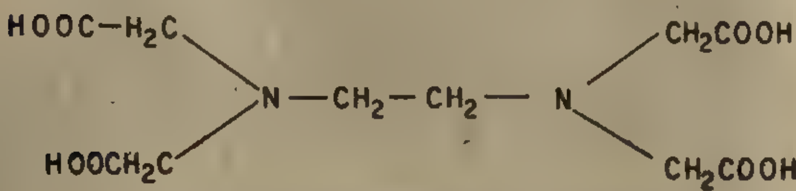


Fig. 10.6. (a) Ethylenediaminetetracetic acid (EDTA).

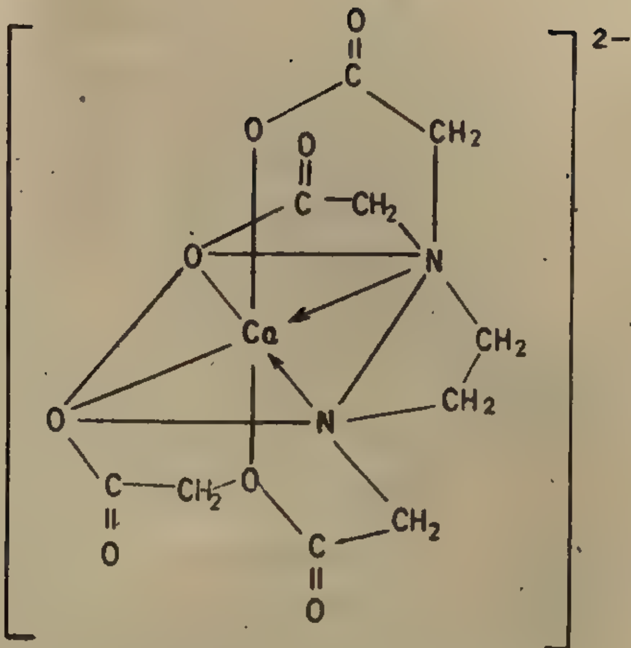
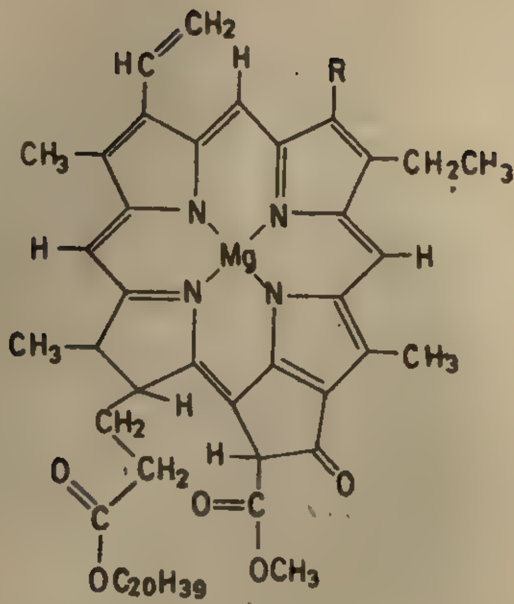


Fig. 10.6. (b) The EDTA complex of calcium.

Chlorophyll (Fig. 10.7), a magnesium complex, is of outstanding importance. The chlorophylls are the green coloured pigments in plants. They absorb visible radiation at 400 nm (violet) and 650 nm (red). The absorbed energy is transferred to active sites within the chloroplast which contains the chlorophyll. At the active sites the energy is used in the photosynthesis of simple sugars from CO_2 and water.

Magnesium forms an important organometallic compound called the Grignard reagent, R–Mg–X. It is made by the reaction of metallic magnesium with the appropriate alkyl or aryl halide in ether.

$$RX + Mg \xrightarrow{\text{Dry ether}} R{-}Mg{-}X$$



$R = -CH_3$; Chlorophyll a

$R = -HC=O$; Chlorophyll b

Fig. 10.7. Chlorophylls

10.4.3. Resemblances between Be and Al (Diagonal Relationship)

The features in which beryllium resembles aluminium (group 13) are listed in Table 10.3.

TABLE 10.3

	Property	*Beryllium*	*Aluminium*
1.	Relative charge density (charge/radius)	64.5 Charge units nm^{-1}	60 Charge units nm^{-1}
2.	Nature of oxide and hydroxide	BeO ; covalent, hard, high melting, insoluble solid, Amphoteric	Al_2O_3 ; covalent, hard, high melting insoluble solid. Amphoteric
3.	Nature of halides (chloride)	Covalent when anhydrous; polymeric bridged structure ; ionizes in water, soluble in organic solvent and acts as Lewis acid.	Covalent (except AlF_3, ionic) when anhydrous ; a bridged dimer Al_2Cl_6 ; ionizes in water and acts as Lewis acid.
4.	Reaction with alkali	Forms the complex $[Be(OH)_4]^{2-}$, the beryllate ion.	Forms the complex $[Al(OH_4]^-$, the aluminate ion.
5.	Reaction with acid	Not easily attacked	Not easily attacked
6.	Complex formation with F^- ions	Forms the complex, $[BeF_4]^{2-}$	Forms the complex $[AlF_6]^{3-}$

10.5. GROUP 13 ELEMENTS : THE BORON FAMILY

Group 13 of the periodic table contains boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). Within the group there is a great variation in basicity. Boron is a non-metal ; the other elements in the group are metals, and so there is a distinct difference in properties between boron and the other elements. These elements are generally less metallic than the corresponding alkaline-earth metals, but as usual, metallic character increases going down the group. Their valence shell electron structure is $ns^2\, np^1$ and generally form compounds with +3 oxidation state. Because of single valence shell p electrons, we might expect the **inert pair effect** to be evident in the observed oxidation states of these elements. As a result, stability of +3 state decreases going down the group. Thallium commonly shows a +1 state. Although +1 compounds of all of them are known.

These elements have smaller atomic radii and higher ionization energies as compared to s block elements of the same period. Their atomic radii and densities show a general increase while boiling points and ionization energies (Table 10.4) experience a drop in value. The difference in the properties of boron and aluminium on the one hand and of both of them from the rest of the members of the group is due to the electronic structure of the penultimate shell.

As seen with s-block elements, boron behaves differently from the other members of the group. Because of its high ionization energy, small size and electronegativity, it forms a large number of covalent compounds (a property common to carbon and silicon) but B^{3+} ion is not known. Boron, in its compounds, has less number of electrons than the maximum possible number, *i.e.*, a total of four electron pair (2s, 2p). Such compounds are called **electron deficient compounds.** It tends to achieve electronic saturation, *i e*, fully occupied outer electron shells, in a variety of ways (Section 10·1). In many respects, the chemistry of boron is similar to that of silicon. The soft, light and very malleable metals (except boron) are widely distributed in nature but only aluminium is abundant. Boron is comparatively less abundant in nature ; it occurs to the extent of about 10 ppm in crystal rocks.

TABLE 10·4 : Properties of group 13 elements

Property	*B*	*Al*	*Ga*	*In*	*Tl*
Atomic number	5	13	31	49	81
Electronic structure	[He] $2s^2$, $2p^1$	[Ne] $3s^2$, $3p^1$	[Ar] $3d^{10}$, $4s^2$, $4p^1$	[Kr] $4d^{10}$ $5s^2$, $5p^1$	[Xe] $4f^{14}$ $5d^{10}$, $6s^2$, $6p^1$
Abundance in earth's crust (ppm)	10	81300	15	1	0.3
Atomic (metallic) radius, r/pm	98	143	135	166	171
ovalent radius, r/pm	82	125	125	144	155
Ionic radius[a] M^{3+}, $r_{M^{3+}}$/pm	27[b]	53·5	62	80	88.5
Melting point, T/K	2573	933	303	429	576
Boiling point, T/K	3923	2740	2676	2273	1730
Density at 293 K ρ/g cm^{-3}	2·34	2.7	5.91	7.3	11.8
Ionization energy, IE/kJ mol^{-1} 1st	800	577	579	558	589
2nd	2427	1816	1979	1820	1970
3rd	3658	2745	2962	2703	2879
Electro-negativity[c]	2.0	1.45	1.8	1.5	1.45
Electron affinity kJ mol^{-1}	−23	−50	—	—	—
Reduction potential at 298 K, $E°$/V					
$M^{3+}(aq)+3e^- \longrightarrow M(s)$	−0.87	−1.66	−0.56	−0.34	+1.26
$M^{+}(aq)+e^- \longrightarrow M(s)$	—	0.55	−0.79 (acid) −1.39 (Alkali)	−0.18	−0.34
Oxidation state	−3 to +3	+1, +3	+1, +3	+1, +3	+1, +3

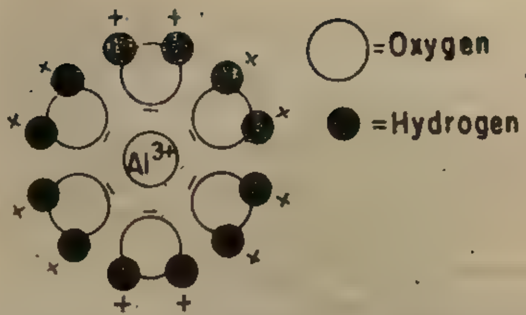
a=6 coordination ; b=normal value ; c=Pauling scale

10·5·1. Chemical Properties of Group 13 Elements and their Trends

We have already stated that the B^{3+} is not known and all its compounds are predominantly covalent as is supported by the intermediate value of electronegativity. The covalent character of the compounds is evidenced by the melting points of chlorides.

BCl_3 = *mp* = 166 K (Covalent) $NaCl$ = *mp* 1074 K (Ionic)

This is because the total ionization energy required to produce a B^{3+} ion is much greater than that compensated by lattice energies (in the case of solids) or by hydration energies (aqueous solution). Hence, ionic compounds containing the B^{3+} ions are not formed and electron-sharing to form covalent bonds is a dominant feature of boron chemistry (Section 10.4). The hydration energies (Fig. 10.8)



$Al^{3+}(g)+6H_2O \longrightarrow [Al(H_2O)_6]^{3+}$ $\Delta H=-4682$ kJ/mol ion

Fig. 10.8. Polar water molecules grouped around an Al^{3+} ion and held by electrostatic attraction giving $[Al(H_2O)]^{3+}$.

of the Al^{3+}, Ga^{3+}, and In^{3+} ions are large enough to compensate for the energy required t‹ remove three electrons, although the reduction potentials become less negative with increasing atomic number (Table 10·4). The value for the formation of Tl^{3+} ions is positive, supporting that Tl^{3+} is less stable than those of the other metals in the group.

The stability of the +3 oxidation state in aqueous solution decreases in the order Al>Ga>In>Tl. But the unipositive (M^+) state assumes importance in going from aluminium to thallium to such an extent that for thallium, the +1 oxidation state is more stable than the +3 oxidation state in aqueous solution.

Elemental aluminium although clearly metallic, shows both ionic and covalent behaviour in its compounds.

$AlCl_3$ =	*mp* 470 K	AlF_3	NaCl=*mp* 1074 K
(Covalent)	(Under pressure)	(Ionic)	(Ionic)

Pure boron is inert and a high temperature is usually required for its reactions ; the other elements, however, are more reactive. All the elements when heated combine with oxygen, nitrogen, halogens and sulphur.

$$4M(s)+3O_2(g) \longrightarrow 2M_2O_3(s)$$
$$2M(s)+N_2(g) \longrightarrow 2MN(s)$$
$$2M(s)+3X_2(g) \longrightarrow 2MX_3(s)$$
$$2M+3S(s, l) \longrightarrow M_2S_3(s)$$

Oxidizing acids (*e.g.*, HNO_3) attack boron slowly ; others have no effect. Aluminium, gallium and indium dissolve in acids with the evolution of hydrogen and the formation of M^{3+} ion.

$$2M(s)+6H^+(aq)+H_2O(l) \longrightarrow 2[M(H_2O)_6]^{3+}+3H_2(g)$$

Inspite of their reactivity, however, Al, Ga and In do not corrode, since the readily formed oxide adheres tightly to the metal protecting it from further attack. The passive character toward HNO_3 is the consequence of the protective oxide coating.

Both Al and Ga dissolve in aqueous alkali forming aluminate and gallate ions which probably exist in solution as $[M(OH)_4]^-$.

$$2M(s)+2OH^-(aq)+6H_2O(l) \longrightarrow 2[M(OH)_4]^-(aq)+3H_2(g)$$
$(M=Al, Ga)$

Boron is not attacked by aqueous alkali, but dissolves in fused alkali.

$$2B(s)+6KOH(l) \longrightarrow 2K_3BO_3(s)+3H_2(g)$$

Boron reacts with many metals to form interstitial metal borides, *e.g.*, MnB_2, TiB_2 MgB_2 and FeB. These metal borides are generally inert but MgB_2 is readily hydrolyzed by dilute acids.

10.5.2. Compounds of Group 13 Elements

Oxides. The oxide, B_2O_3 (a product of combination of boron and oxygen) is obtained as a glass-like solid on heating orthoboric acid.

$$2B(OH)_3 \longrightarrow B_2O_3+3H_2O$$

It is acidic in nature and dissolves in water to give H_3BO_3. It forms complex borate glasses with other metal oxides, on fusion. It resembles to silica (SiO_2) in physical properties.

Hydrated alumina, $Al_2O_3.2H_2O$ is the natural bauxite mineral. Pure alumina is prepared by heating $Al(OH)_3$ or ammonium alum. It is also obtained by heating the metal in air. Reactions of metallic aluminium at room temperature are slowed considerably by the formation of a surface skin of Al_2O_3.

Pure Al_2O_3 is colourless (or white if powdered) but when Cr^{3+} ions substitute for some of the Al^{3+} ions, a red colour is produced, as in the gemstone ruby.

Alumina is amphoteric in nature. Its freshly prepared sample reacts with both acids and alkalis.

$$Al_2O_3(s)+6H^+(aq) \longrightarrow 2Al^{3+}(aq)+3H_2O(l)$$
$$Al_2O_3(s)+2OH^-(aq)+3H_2O \longrightarrow 2[Al(OH)_4]^-(aq)$$

Alumina is used (*i*) as a refractory material and for the internal lining of the furnaces; (*ii*) as an adsorbing stationary phase in column chromatography; and (*iii*) as a dehydrating agent.

$$CH_3CH_2OH \xrightarrow[573K]{Al_2O_3} CH_2{=}CH_2+H_2O$$

Hydroxides. The hydroxide of boron, $B(OH)_3$ being acidic in nature is called **orthoboric acid**. It is obtained by hydrating B_2O_3. The hydrolysis of various compounds such as halides, hydrides, esters, *etc.* also gives the acid.

$$BCl_3+3H_2O \longrightarrow H_3BO_3+3HCl$$

Boric acid can also be processed from natural sources. Aqueous solution of borax on treating with concentrated HCl gives flaky crystals on cooling.

$$Na_2B_4O_7+2HCl+5H_2O \longrightarrow 2NaCl+4H_3BO_3$$

Boric acid is a white crystalline solid. In dilute solutions, boric acid acts as a Lewis acid (OH^- acceptor) rather than as a proton donor :

$$B(OH)_3+2H_2O \longrightarrow [B(OH)_4]^-+H_3O^+(p^k=9.00)$$

It gets polymerized in concentrated solution :

$$3B(OH)_3 \longrightarrow [B_3O_3(OH_4)_4]^- + H_3O^+ + H_2O$$

It behaves as a weak monobasic acid :

$$B(OH)_3 \longrightarrow H_3BO_3 \longrightarrow H^+H_2BO_3^- \longrightarrow H_3O^+ + BO_2^-$$

Some reactions of boric acid are shown below :

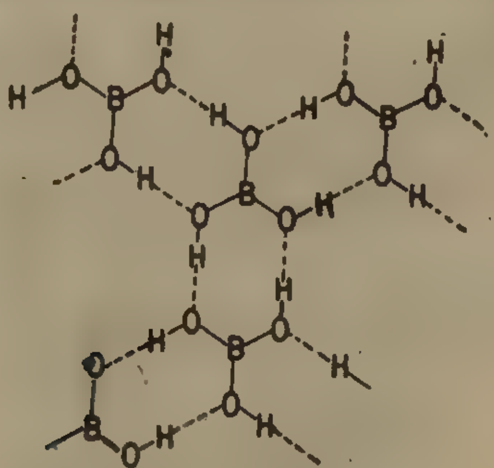
$$B(OH)_3 \xrightarrow[\text{metal oxides}]{\text{Fusion with}} \text{Borates}$$

$$B(OH)_3 \xrightarrow{NH_4HF_2} NH_4BF_4 \xrightarrow[\text{Heat}]{B_2O_3} BF_3$$

$$B(OH)_3 \xrightarrow{\text{Alcohols}+H_2SO_4} B(OR)_3$$

$$B(OH)_3 \xrightarrow[-H_2O]{\text{Heat, 373 K}} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{\text{Heat, 423 K}} \underset{\text{Tetraboric acid}}{H_2B_4O_7} \xrightarrow[\text{Fuse}]{\text{Red heat}} B_2O_3 \xrightarrow[\text{Heat}]{\text{Alcohols}} B(OR)_3$$

In the boric acid, each B atom is bonded to three oxygen atoms, arranged at the corners of an equilateral triangle. Thus, it assumes a layer structure of planar $B(OH)_3$ units linked together by hydrogen bonding as shown in Fig. 10.9.



Hydrogen bonding
(Broken lines)

Fig. 10.9. Layer structure of orthoboric acid, hydrogen bonds are represented by lines.

Aqueous solution of boric acid is commonly used as a mild antiseptic. Boric acid also finds use in the manufacture of heat and chemical resistant borosilicate glass (*e.g.*, pyrex) and certain optical glasses.

Aluminium hydroxide and other group 13 metal hydroxides are insoluble in water and form gelatinous precipitate. Alumina dissolves in alkali to form the aluminate ion, $[Al(OH)_4]^-$. Its solution on seeding with $Al(OH)_3$ and agitating with air results in precipitation of $Al(OH)_3$.

$$Al_2O_3(s)+2OH^-+3H_2O \longrightarrow 2[Al(OH)_4]^-$$

$$[Al(OH)_4]^- \longrightarrow Al(OH)_3(s)+OH^-$$

Carbon dioxide present in air, being acidic, aids in the precipitation.

$$[Al(OH_4]^-+CO_2 \longrightarrow Al(OH)_3(s)+HCO_3^-$$

Addition of a limited amount of alkali to a solution containing Al^{3+}, precipitates $Al(OH)_3$. The freshly precipitated hydroxide is not stoichiometrically well characterized, and it is more correctly referred to as hydrous aluminium oxide, $Al_2O_3.xH_2O$.

Aluminium hydroxide is amphotoric, and so it dissolves in excess base.

$$Al(OH)_3(s)+OH^- \longrightarrow [Al(OH)_4]^-$$

In qualitative analysis, while precipitating Al^{3+} as $Al(OH)_3$, addition of aluminon dye (or litmus solution) forms a red lake. This is the basis of detection of Al^{3+} ion in analysis.

Hydrides. Boron forms a series of volatile covalent molecular compounds with hydrogen. In some respects, they resemble the hydrides of carbon and silicon. In view of its trivalency, it is expected to form a simple hydride BH_3. However, the simplest known and stable hydride is diborane, B_2H_6 (BH_3 is very unstable). Boron does not react directly with hydrogen. The boron hydrides are sometimes called **boranes** by analogy with the alkanes (hydrocarbons). Two series of boranes, B_nH_{n+4} and B_nH_{n+6} are particularly important.

Diborane is made by treating sodium borohydride, $NaBH_4$, with concentrated H_2SO_4 and other non-aqueous acids (H_3PO_4). Generally $NaBH_4$ is obtained from trimethyl borates and sodium hydride, *i.e.*,

$$4H^- + B(OMe)_3 \xrightarrow{523\text{ K}} BH_4^- + 3OMe^-$$

$$2NaBH_4+H_2SO_4 \longrightarrow Na_2SO_4+B_2H_6$$

Diborane can also be obtained by action of hydrogen on boric oxide.

$$B_2O_3+6H_2 \xrightarrow[Al_2Cl_6]{\text{Al or}} B_2H_6+3H_2O$$

Diborane is prepared on an industrial scale by the reaction of lithium hydride with BF_3.

$$2BF_3(g) + 6LiH(s) \xrightarrow{450\ K} B_2H_5(g) + 6LiF(s)$$

In the laboratory, it is made by the reaction of iodine with sodium borohydride in a high boiling polyether solvent, *e.g.*, $(MeOCH_2CH_2)_2O$.

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

Diborane is a colourless gas Its reactions (also based upon its electron deficient nature are given in Fig. 10.10. Pyrolysis (373-523 K) of B_2H_6 is the source of other higher hydrides. Most of the boranes catch fire on exposure to air and are readily hydrolyzed by water.

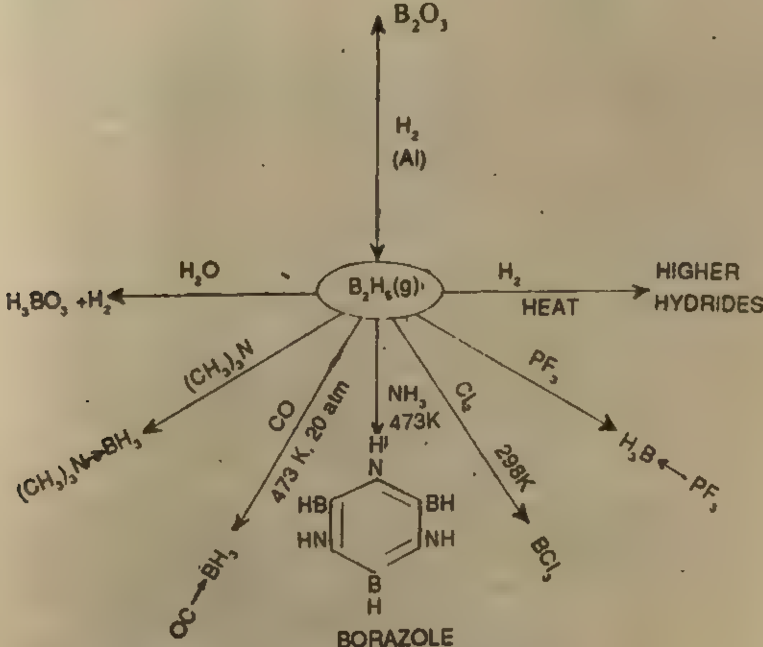


Fig. 10.10. Some reactions of diborane, B_2H_6

Boron also forms various types of borohydride ions, the most important of which is the tetrahedral $[BH_4]^-$. Borohydrides are prepared by the reaction of alkali metal hydrides with B_2H_6 in diethyl ether.

$$2MH + B_2H_6 \longrightarrow 2M^+[BH_4]^-$$
$$M = Li \text{ or } Na$$

Borohydrides are used as reducing agents. $NaBH_4$ on treatment with H_2SO_4 gives diborane (discussed above).

Since boron has one electron less than carbon, diborane cannot be structurally identical with ethane, C_2H_6, because it is electron deficient.

Diborane has been found to possess a bridge structure (Fig. 10.11) ir which each B atom is bonded to two H atoms (called terminal H atoms) by regular electron-pair bonds. The resulting BH_2 fragments are bridged by two H atoms (evidenced by electron diffraction and Raman and infrared spectroscopy). The bridge H

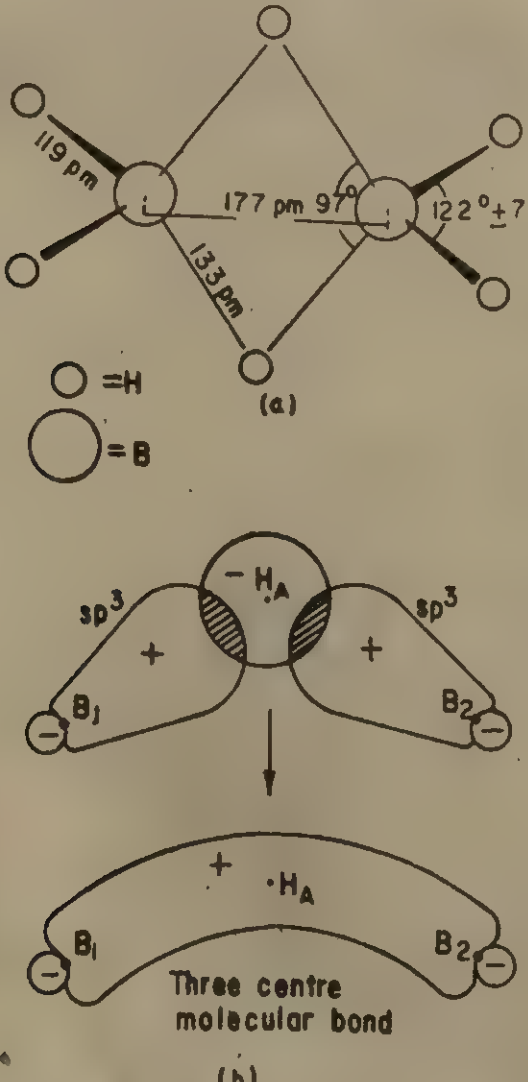


Fig. 10.11. (a) Bridge structure of diborane.
(b) Three centre bonds in diborane.

atoms are in a plane perpendicular, *i.e.*, one above and one below the plane to the rest of the molecule. If we consider the bonding situation in B_2H_6, there are eight B–H bonds but only twelve valence electrons. Obviously, there are not enough electrons to form eight normal two-centre two-electron (2c–2e) or electron pair bonds. Bonding in diborane and other boranes is described in terms of multicentre bonds.

The nature of bonds in hydrogen bridges is now well established. The two hydrogen bridges involve a total of four electrons, one electron from each hybrid boron atom and one from each hydrogen atom. An sp^3 hybrid orbital from each boron atom overlaps the 1s orbital of the hydrogen atom giving a delocalized orbital containing one pair of electrons but covering all the three nuclei. This makes one of the bridges. This is known as **three centre electron pair bond**, B-H-B. The molecule of diborane contains two such bonds. Due to repulsion between the two hydrogen nuclei, the delocalized orbitals or bridges are bent away from each other in the middle. This is why the hydrogen bridge. One orbital is shifted upwards in the middle and the other bridge orbital will be shifted downwards.

Other members of the group also form a few stable hydrides. Aluminium forms a solid polymeric hydride of formula $(AlH_3)_n$ called **alane** when aluminium chloride in dry ether as treated with lithium hydride.

$$3LiH + AlCl_3 \xrightarrow{\text{Dry ether}} AlH_3(s) + 3\,LiCl$$

This hydride is stable up to 373K, but decomposes into aluminium and hydrogen at higher temperatures. An isolable solid complex hydride stable to about 398K and ether soluble hydride is formed with excess of lithium hydride.

$$4LiH + AlCl_3 \xrightarrow{\text{Dry ether}} LiAlH_4 + LiCl$$

Great chemical reactivity of alane makes its synthesis by hydrolysis reactions difficult. It is also prepared by subjecting a mixture of trialkyls, $Al(CH_3)_3$, and hydrogen to a high voltage electric glow discharge.

It hydrolyzes violently to yield aluminium hydroxide and hydrogen gas. It is a strong reducing agent. Alane also acts as a Lewis acid and its adducts with ammonia and other reagents have been identified.

Halides. All the group 13 elements form the trihalides, MX_3. Boron forms the halides BX_3 (X=F, Cl, Br, I). The method of formation of the last three is by reduction of the oxide with carbon in the persence of the appropriate halogen at high temperature. The action of HF on B_2O_3 is used to prepare the fluoride.

All boron halides are covalent molecules and exist as planar triangular (sp^2 hybridization) monomers in the vapour phase. On hydrolysis they give orthoboric acid.

$$4BF_3+3H_2O \longrightarrow H_3BO_3+3HBF_4$$

$$BX_3+3H_2O \longrightarrow H_3BO_3+3HX \text{ (H=Cl, Br, or I)}$$

Boron trihalides behave as acceptor molecules and form many addition compounds with compounds having nitrogen and oxygen as donor atoms in particular, *e.g.*, amines, ethers, *etc.*

$$F_3B \longleftarrow NH_3 \text{ and } F_3B \longleftarrow O(C_2H_5)_2$$

As a consequence of its strong Lewis acid character, BF_3 is used as a catalyst in several industrial processes.

Their relative acceptor strength or Lewis acidity generally follows the order : $BI_3 > BBr_3 > BCl_3 > BF_3$.

Aluminium forms both monohalides (AlX) and trihalides (AlX_3). Monohalides are short lived only in gas phase. Table 10.5 shows a comparison of some properties of the aluminium halides.

TABLE 10.5 : A comparison of aluminium trihalides

Property	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
Melting point, T/K	1563	466	370.5	462.4
Boiling point, T/K	Sublimes above *mp*	Sublimes at 450K	528	654
Heat of formation ΔH°_f/kJ mol^{-1}	1498	707	527	310
Condition for hydrolysis	Steam	Water	Water	Water
Solubility in water	Insoluble	Readily soluble	Readily soluble	Readily soluble
Solubility in organic solvent	Soluble	Soluble	Soluble	Soluble

The distinct change in the properties from fluoride to iodide is because of ionic nature of fluoride to covalent structures (triodide is typically covalent).

AlF_3 is produced by treating Al_2O_3 with HF gas at 473K and the other trihalides are made by the direct exothermic combination of the elements.

Aluminium chloride is prepared by dissolving aluminium metal, its oxide or hydroxide in hydrochloric acid. It crystallizes out from aqueous solution as a hydrate. $AlCl_3.6H_2O$ or better $[Al(H_2O)_6].Cl_3$. The hydrate decomposes on heating.

$$2AlCl_3.6H_2O \longrightarrow Al_2O_3+6HCl+3H_2O$$

To prepare anhydrous sample of $AlCl_3$, dry chlorine or HCl gas is passed over heated aluminium powder.

$$2Al+3Cl_2 \longrightarrow 2AlCl_3$$

$$2Al+6HCl \longrightarrow 2AlCl_3+3H_2$$

Anhydrous $AlCl_3$ is a white crystalline deliquescent substance soluble in organic solvents. It fumes in air.

Anhydrous aluminium chloride is a three dimensional polymeric solid in which chlorine atoms form bridges between adjacent aluminium atoms. It sublimes at 450K (1 atm) forming vapours which consist of Al_2Cl_6 dimers (Fig. 10.12). Each molecule uses two of its six Cl atoms to 'bridge bond' the two Al atoms. Above 673K it dissociates.

$$Al_2Cl_6\,(g) \rightleftharpoons 2AlCl_3(g)$$

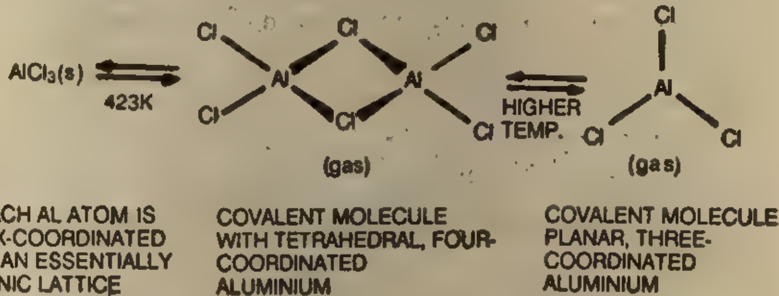


Fig. 10.12. Effect of temperature on $AlCl_3$.

The AlX_3 structures (trigonal, sp^2 hybridization) have a vacant orbital and are Lewis acids. $AlCl_3$ accepts electrons in this orbital to form structures with tetrahedral aluminium (sp^3 hybridized) such as the dimer Al_2Cl_6 in the liquid and solid states, the tetrachloroaluminate anion $[AlCl_4]^-$, and adducts with Lewis bases, *e.g.*, NH_3, PH_3, $COCl_2$ *etc.*

Anhydrous aluminium chloride is used as a catalyst in the Friedel Crafts reaction. It is used in petroleum cracking and in the manufacture of dyes, drugs and perfumes.

Oxyanion salts : Most of the salts of group 13 elements are soluble in water, but extensive reaction of the M^{3+} ions with water takes place :

$$[M(H_2O)_6]^{3+}(aq)+H_2O(l) \longrightarrow [M(H_2O)_5OH]^{2+}(aq)+H_3O^+(aq)$$

The solutions are sufficiently acidic that anions of weak acids (such as acetate, sulphide, cyanide (carbonate) cannot exist.

$$CO_3^{2-}(aq)+2H_3O^+(aq) \longrightarrow CO_2(g)+3H_2O(l)$$

Aluminium sulphate, $Al_2(SO_4)_3.10H_2O$ (hair salt or feather alum) is prepared industrially by treating bauxite or clay with conc. H_2SO_4.

$$Al_2O_3\,.\,SiO_2+3H_2SO_4 \longrightarrow Al_2(SO_4)_3+3H_2O+2SiO_2$$

The residue is extracted with water, filtered and recrystallized.

Aluminium was first discovered in a series of salts known as **alums**. These are hydrated sulphates containing both uni- and tripositive ions.

$$M_2^I(SO_4) \cdot M_2^{III}(SO_4)_3 \cdot 24H_2O$$

where $M^I = Na^+, K^+, Rb^+, Cs^+, NH_4^+, Tl^+$, or Ag^+
and $M^{III} = Al^{3+}, Fe^{3+}, Cr^{3+}$, *etc.*

Some of the well known alums are :

Potash alum	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Ferric alum	$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$
Chrome alum	$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

To prepare an alum, hot equimolar saturated solutions of the two metal sulphates are mixed up and the solution is allowed to cool. Crystals are seen after some time. Alums are used to purify water and as mordants in dyeing. Vast quantities of alums are used in the paper and dye industries. They act as styptics to stop bleeding.

Complexes : Aluminium (III) forms complexes with oxalic acid $[Al(C_2O_4)_3]^{3-}$, and 8-hydroxyquinoline, $Al(C_9H_6ON)_3$. The latter reaction is used in the quantitative estimation of aluminium in solution.

Among organoaluminium compounds, aluminium alkyls (R_6Al_2) are the most important, which are reactive liquids.

$$3R_2Hg + 2Al \longrightarrow 2R_3Al + 3Hg$$

10.5.3. Diagonal Relationship between Boron and Silicon

Boron shows more resemblance to silicon with which it forms a diagonal relationship, than to aluminium, as shown below :

(*i*) **Non-metallic character.** Boron and silicon are typical non-metals. They both have high melting points.

(*ii*) **Allotorpy.** Both these elements exhibit allotropy. They exist in two well known forms, the amorphous and crystalline. Crystalline boron and silicon are hard.

(*iii*) **Density and atomic volume and electronegativity.** The densities and the atomic volumes of both the elements are low. Their electronegativity is almost similar B=2.0 ; Si=1.8.

(*iv*) **Hydrides.** Both boron and silicon form a number of covalent hydrides which have identical methods of preparation and similar properties. These are volatile, spontaneously inflammable and readily hydrolyzed.

(*v*) **Oxides.** Boron and silicon burn in air to form oxides, B_2O_3 and SiO_2, which are stable and acidic. The oxides in association with water yield corresponding acids, boric and silicic acids. Both are weak acids. Both the oxides are covalent macromolecular, glassy solids.

(*vi*) **Halides.** Both boron and silicon burn in halogens to form the halides. The fluorides of both are colourless fuming gases.

The chlorides, BCl_3 and $SiCl_4$ are liquids which are hydrolyzed by water to acids. All the halides are covalent and completely hydrolyzed by water.

(*vii*) **Action of alkalis.** Both the elements and their oxides dissolve in alkalis to form borates and silicates with the liberation of hydrogen. Borates and silicates have tetrahedral BO_4 and SiO_4 structural units, respectively. Borosilicates are known in which boron can replace silicon in the three-dimensional lattice. However, boron can also form planar BO_3 units.

(*viii*) **Both elemental boron and silicon are semiconductors.** Aluminium, on the other hand, is a metallic conductor.

(*ix*) **Reaction with metals.** Both elements form binary compounds with metals, *e.g.*, Ca_3B_2 (boride) and Mg_2Si (silicide). Some of the borides and silicides undergo hydrolysis to yield boranes and silanes respectively.

10.6. GROUP 14 ELEMENTS : THE CARBON FAMILY

Group 14 of the periodic table contains carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). The elements range from non-metallic carbon, through semi-metallic silicon and germanium to the weakly electropositive metals tin and lead. The properties of the elements (Table 10·6) show the expected trends for a related family of elements in the periodic table. Their valence shell electron structure is ns^2np^2. Group 14 elements can lose or share the two p electrons to exhibit +2 oxidation state, or they may share all four valence electrons to exhibit +4 oxidation state. The stability of the lower oxidation state increases going down the group. This is called the inert pair effect, since the two s electrons remain nonionized or unshared for the +2 oxidation state; $PbCl_2$ is more stable than $PbCl_4$. The values of electronegativity and ionization energy indicate that there must be a considerable degree of covalency in the chemical bonding of these elements. On account of high ionization energies, simple M^{4+} ions of the group are not known. The tendency to form negative ions by gaining electrons is also not observed except in the case of carbon, *i.e.*, in ionic carbides of electropositive metals. Both tin and lead in +2 oxidation state tend to form ionic compounds. The group 14 elements attain the noble gas configuration by forming four covalent bonds utilizing sp^3 hybrid orbitals (CCl_4, $SiCl_4$, $PbCl_4$, *etc.*).

The covalency of carbon is limited to four because of the absence of d oribitals whereas the other elements show a covalency higher than four because here d orbitals are available for bonding. This explains the inertness of CCl_4 towards water compared with the ready hydrolysis shown by the tetrahalides of the succeeding elements.

Carbon differs from the rest of the elements of the group because of its small size, high electronegativity, and non-availability

of d orbitals. It exhibits the unique property of **catenation**, *i.e.*, forming chains and rings of identical atoms. This property of self-linkage is of an exceptional degree in carbon but exists to a relatively small degree in silicon also. Hydrides with chains of 10 silicon atoms have been made. This property is related to the strength of the M—M bond. The higher the bond energy, the greater will be the tendency to form chains. (C—C bond energy = 348 kJ mol^{-1}, Si—Si bond energy = 226 kJ mol^{-1}). Among group 14 elements, carbon has another distinct property of forming $p\pi - p\pi$ multiple bonds to itself and to other elements, particularly nitrogen and oxygen. Thus, compounds containing C=C, C≡C, C=O, C=N, C≡N and C=S functional groups are numerous. Analogous compounds of silicon and the heavier members of the group are largely unknown. Recently, a few compounds containing double bonds between two silicon, germanium or tin atoms or between a silicon and a carbon atom have been isolated.

TABLE 10.6 : Properties of group 14 elements

Property	*C*	*Si*	*Ge*	*Sn*	*Pb*
Atomic number	6	14	32	50	82
Electronic configuration	[He] $2s^2 2p^2$	[Ne] $3s^2 3p^2$	[Ar] $3d^{10} 4s^2, 4p^2$	[Kr] $4d^{10} 5s^2 5p^2$	[Xe] $4f^{14} 5d^{10}, 6s^2, 6p^2$
Atomic radius, r/pm	91	132	137	162	175
Covalent radius[a], r/pm	77	117	122	140	154
Ionic radius[b], M^{2+} $r_{M^{2+}}$/pm	—	—	73	118	120
Ionic radius[b], M^{4+}, $r_{M^{4+}}$/pm	—	40	53	69	146
Density at 293K, ρ/g cm^{-3}	2.22 (graphite) 3.51 (diamond)	2.33	5.32	7·3	11.3
Ionization energy, IE/kJ mol^{-1} 1st :	1086	786	761	708	715
2nd :	2352	1577	1537	1411	1450
3rd :	4620	3228	3300	2942	3081
4th :	6220	4354	4409	3929	4082
Electronegativity	2.5	1.8	1·8	1·8	1.9
Melting point, T/K	4273	1693	1218	505	600
Boiling point, T/K	—	3653	3123	3396	5124
Electrode potentials at 298K, E°/V $M^{2+}(aq) + 2e^- \longrightarrow M(s)$	—	—0·84	—0·30	—0·136	—0·130
Oxidation states	—4, —1	4	4	+2(+4)	+2(+4)
Abundance in earth's crust (ppm)	320	277, 200	7	40	16

[a]for M^{IV} Oxidation state ; [b]6-Coordination ; [c]Pauling scale

The notable tendency of carbon to form $p\pi-p\pi$ multiple bonds is reflected in the structure of its allotropic modification graphite, which may be contrasted with the structure of diamond (Unit 6, Class XI textbook). In both forms, carbon atoms are linked by a network of covalent bonds so that a giant molecule results. Such a structure is responsible for the high melting point of the allotropes of carbon since in order to overcome the rigidity of the structure, it is necessary to break C—C bonds. In diamond, each carbon atom is linked tetrahedrally to four other carbon atoms by the overlapping of sp^3 hybrid orbitals [Fig. 10.13 (*a*)]. Graphite consists of planar hexagonal layers of carbon atoms [Fig. 10.13 (*b*)] held together by relatively weak van der Waals forces. Within each layer, a carbon atom is bonded to three other carbon atoms by the sideways overlapping of sp^2 hybrid orbitals and the unhybridized p orbitals from each carbon to give extended delocalized π-bonding system encompassing the entire layer. The electron mobility imparted by delocalization is responsible for the conductive properties of graphite.

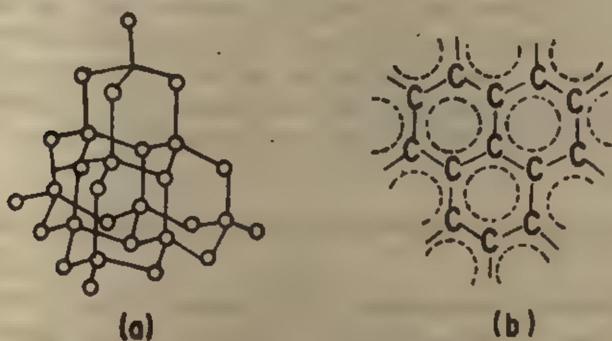


Fig. 10.13. Linkage of carbon atoms in (a) diamond, and (b) graphite.

Silicon, germanium and the grey allotrope of tin possess the diamond structure. The graphite structure is not adopted by the elements because of the inability of the atoms to form $p_\pi - p_\pi$ bonds with each other. However, the mechanical hardness of the elements decreases from silicon onwards because of the weaker covalent bonding between the atoms of heavier elements. That is why the Si—Si bonds are longer than the C—C bonds, and so the melting point and boiling point of silicon are lower than those of carbon (Table 10.6).

Silicon forms much stronger bonds with oxygen, flourine, and chlorine than with itself or hydrogen (Table 10·7). In contrast to

the hydrocarbons, the silicon compounds with Si—Si or Si—H bonds are generally reactive, *e.g.*, hydrides of silicon, silanes.

TABLE 10.7 : Bond energies involving carbon and silicon

Bond	*Energy/kJ*	*Bond*	*Energy/kJ*
C—C	348	Si—Si	226
C—H	414	Si—Si	318
C—O	360	Si—O	464
C—F	389	Si—F	598

There is evidence for multiple bonding between silicon and oxygen or nitrogen. For example, the geometry around the nitrogen atom in trimethylamine, $N(CH_3)_3$ is pyramidal while the analogous silicon compound, $N(SiH_3)_3$ assumes a planar arrangement of its three bonds. In the latter, the lone pair of electrons on the nitrogen is transferred to an empty d orbital in silicon (more accurately described as $p\pi - d\pi$ bonding) thereby NSi_3 unit assumes planarity (Fig. 10.14).

10.6.1. Chemical Properties of Group 14 Elements and their Trends

The chemical reactivity of the elements increases from carbon to tin ; lead is rather less reactive than tin. When heated, the elements combine with reagents such as oxygen and the halogens, and in doing so, usually utilise all the valence electrons (except Pb, which shows inert pair effect).

Reactivity of the elements is frequently protected by surface coating. Lead, for example, forms under different conditions, a layer of slightly soluble oxide, basic carbonate, chloride or sulphate which limits further attacks. Some representative reactions of the elements. are given in Table 10.8. Silicon is only attacked by one acid, *viz.*, HF and this presumably because of the stability of the final product, $[SiF_6]^{2-}$.

$$Si + 4HF \longrightarrow SiF_4 + 2H_2$$

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

TABLE 10.8 : Reactions of group 14 elements

	Reagent	*Reaction*	*Comment*
1.	Oxygen or air	$M+O_2 \longrightarrow MO_2$	Pb is attacked slowly and PbO is formed ; Sn is attacked at its mp.
2.	H_2O (room temperature)	$Pb+H_2O \xrightarrow{O_2} Pb(OH)_2$ (in soft water)	
		$Pb+H_2O \xrightarrow{O_2}$ Insoluble $PbSO_4$ and $PbCO_3$ (in hard water)	Sulphate and carbonate present in hard water react with $Pb(OH)_2$ forming insoluble $PbSO_4$ and $PbCO_3$. Ge and Sn are not attacked by H_2O.
3.	Steam	$M+2H_2O \longrightarrow MO_2+2H_2$	
4.	Sulphur	$M+S_2 \longrightarrow MS_2$	Lead forms PbS
5.	Chlorine	$M+2Cl_2 \longrightarrow MCl_4$	Lead gives $PbCl_2$
6.	Aqueous alkali (hot and conc.)	$Sn+NaOH \longrightarrow Na_2SnO_3+H_2$	Reaction is slow
		$Na_2SnO_3+2H_2O \longrightarrow Na_2[Sn(OH)_4]$	
		$Pb+2NaOH \longrightarrow Na_2PbO_2+H_2$	
		$Pb+4KOH+2H_2O \longrightarrow K_4[Pb(OH)_6]+H_2$	
		$Si+2OH^-+H_2O \longrightarrow SiO_3^{2-}+2H_2$	Carbon does not react
7.	Acids		
	(*i*) Cold and dilute HCl	$Sn+2HCl \longrightarrow SnCl_2+H_2$	Sn reacts very slowly. Pb hardly reacts.
	(*ii*) Hot conc. HCl	$Sn+2HCl \longrightarrow SnCl_2+H_2$	With Pb slow reaction due to the formation of insoluble $PbCl_2$
	(*iii*) Hot conc. H_2SO_4	$Sn+2H_2SO_4 \longrightarrow SnSO_2+2SO_2+4H_2O$	Ge also reacts
		$Pb+2H_2SO_4 \longrightarrow Pb(HSO_4)_2+H_2$	Lead reacts vigorously
		$C+2H_2SO_4 \longrightarrow CO_2+SO_2+2H_2O$	
	(*iv*) Hot conc. HNO_3	$3M+4HNO_3 \longrightarrow 3MO_2+4NO+2H_2O$	Lead forms PbO : reaction is possible with Ge and Sn
	(*v*) Dilute HNO_3	$4Sn+10HNO_3 \longrightarrow 4Sn(NO_3)_2+NH_4NO_3+3H_2O$	
		$3Pb+8HNO_3 \longrightarrow Pb(NO_3)_2+2NO_2+2H_2O$	
8.	Metals		Form alloys

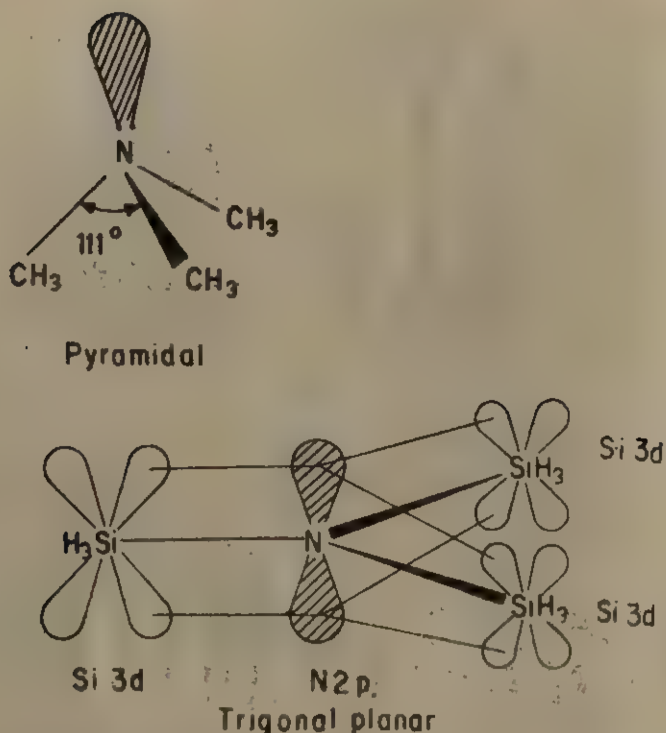


Fig. 10.14. Shapes of $(CH_3)_3N$ and $(SiH_3)_3N$

10.6.2. Compounds of Group 14 Elements

Oxides : All group 14 elements form oxides of composition MO_2 but there exists differences among their structures and properties.. Monoxides of the type MO except SiO are also known.

Of all the group 14 oxides, the carbon oxides are most unique. Both carbon monoxide and carbon dioxide are gases at room temperature while the other group 14 oxides are all solids with high melting points. This difference seems to be because of the presence of π bonds in the carbon compounds. In carbon dioxide, O=C=O valence requirement of both carbon and oxygen is satisfied, hence, the molecule is molecular. Since CO_2 molecule is linear and has no dipole moment, the intermolecular forces are solely van der Waals forces. The π bonding is, however, unfavourable for Si, Ge, Sn and Pb ; therefore, in their dioxides, MO_2 valence requirement of both the atoms is met by single bonds. Thus, these oxides are a three-dimensional covalent network solid in which each elemental atom is bound to four oxygens and each oxygen to two similar atoms *e g.*, two silicon atoms (Fig. 10.15).

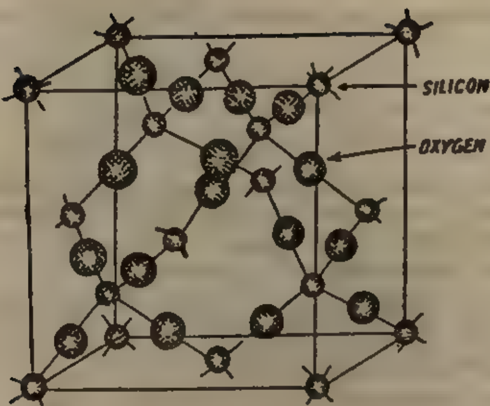


Fig. 10.15. The silicon dioxide structure.

Silica, SiO_2 exists in three crystalline forms which are stable at different temperatures. These are (*i*) quartz, (*ii*) tridymite and (*iii*) cristobalite. Thermodynamically, quartz is the most stable form, Since their interconversion is very slow, all the three forms are found in nature.

$$\text{Quartz} \xrightarrow{1143\ K} \text{Tridymite} \xrightarrow{1743\ K} \text{Cristobalite} \xrightarrow{1983\ K} \text{Liquid } SiO_2$$

All the dioxides of group 14 have acidic properties, but on descending the group there is a marked decrease in this property. GeO_2, SnO_2 and PbO_2 are amphoteric in nature.

Both CO and CO_2 are formed when carbon is burned in air. Carbon dioxide is essential to a number of biological processes such as respiration, photosynthesis and the regulation of the pH of the blood. It acts as a Lewis acid with water to form the weak electrolyte carbonic acid.

$$CO_2+H_2O \rightleftharpoons H_2CO_3$$

Silicon (IV) oxide is much less reactive than carbon dioxide, but like that compound, it is an acidic oxide. Thus, SiO_2 on heating with concentrated sodium hydroxide solution or molten sodium hydroxide forms sodium silicate.

$$SiO_2(s)+2NaOH(aq) \longrightarrow Na_2SiO_3(aq)+H_2O(l)$$

Silica can be regarded as the anhydride of $Si(OH)_4$. It is insoluble in water and melts at 1983 K to form a viscous liquid which on cooling forms glass (fused silica). Silica glass is used for the manufacture of vessels used in the laboratory and industry. Silica also reacts with fluorine and hydrofluoric acid. The reaction with hydrofluoric acid is used in qualitative detection of silica or

silicates. Certain gems, *e.g.*, amethyst also consists of silica coloured by impurities.

Sn (IV) oxide occurs naturally as tinstone. It is generally obtained by heating the element with conc. HNO_3.

$$3Sn + 4HNO_3 \rightarrow 3SnO_2 + 4NO + 2H_2O$$

It is hydrolyzed by water forming an insoluble hydrous oxide $SnO_2.2H_2O$ [often represented as $Sn(OH)_4$.]. It dissolves in excess base to form the water soluble stannate, Na_2SnO_3. Tin dioxide is used to prepare white glasses and enamels.

Lead (IV) oxide is prepared by oxidizing Pb (II) compound in alkaline medium. Pb $(OH)_2$ being amphoteric in nature dissolves in excess base to form the plumbite ion.

$$Pb(OH)_2(s) + OH^-(aq) \rightarrow Pb(OH)^-_3(aq)$$

Plumbite ion on oxidizing with hypochlorite gives Pb (IV)O_2.

$$Pb(OH)_3^- + OCl^- \rightarrow PbO_2(s) + OH^- + Cl^- + H_2O$$

Lead dioxide interacts with alkali to form plumbates. It is an effective oxidizing agent, liberating Cl_2 from HCl and oxidizing Mn^{2+} in acid solution to MnO^-_4. With nitric acid it reacts forming Pb (II) salts with liberation of oxygen.

$$PbO_2 + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O + \tfrac{1}{2}O_2$$

It is a chief constituent of the anode of the charged lead accumulator.

Amongst the group 14 monoxides, carbon monoxide (CO) is the most important. It is a gas at room temperature and is isoelectronic with nitrogen. It has the highest bond energy (1070 kJ mol^{-1}) among diatomic molecules. A molecular orbital description suggests the presence of a triple bond (:C$\leftarrow$O :), between carbon and oxygen. It can also be considered in terms of resonance of the following canonical forms :

$$\overset{+}{:C}\ \overset{-}{:\ddot{O}:} \leftrightarrow :C::\ddot{O} \leftrightarrow \overset{-}{:C}:::\overset{+}{O:}$$

Carbon monoxide acts as a ligand and combines with many transition metal atoms (in their low oxidation states) to give **metal carbonyls** and related compounds. *e.g.*, $Ni(CO)_4$, $Fe(CO)_5$ and $Cr(CO)_6$. In these compounds, carbon is bonded to the transition metal and hence they are classified as organometallic compounds which we shall discuss in Unit 12. It is a colourless gas which has reducing properties. Many metal oxides are reduced to the metal as, for example, in the following reaction :

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

With chlorine it gives carbonyl chloride (phosgene), a poisonous gas.

Tin and lead form SnO and PbO which are essentially basic. Lead also forms the oxide Pb_3O_4, 'red lead'; this compound contains Pb(II) and Pb IV) species and behaves in many respects as a mixture of PbO and PbO_2.

Hydrides : The formation of volatile hydrides is a property associated with non-metals and carbon is the supreme example. Compared with the enormous number of hydrocarbons, only a few **silanes** and **germanes** are known and the weakly electropositive metals tin and lead form only **stannane** (SnH_4) and **plumbane** PbH_4. Binary hydrides of Si and Ge have the general formula M_nH_{2n+2} (M=Si and Ge). The first six or seven homologues in each series have been identified. They are obtained when magnesium silicide or germanide is treated with dilute acid, though monosilane is conveniently prepared by the reduction of $SiCl_4$ by $LiAlH_4$ in diethyl ether at 273K. Both GeH_4 and SnH_4 are made by similar reactions. PbH_4 is obtained in small quantities when an alloy of magnesium and thorium-B (radioactive Pb-212) is hydrolyzed by dilute acid.

The thermal stability of the hydrides falls off rapidly with increasing molecular mass. The stability towards water, however, follows the order :

$$CH_4 > GeH_4 > SnH_4 > SiH_4$$

The silanes are unlike hydrocarbons in many respects. Differences arise because of (*i*) the availability of d orbitals for silicon, and (*ii*) the lower electronegativity of silicon than carbon. In fact Si—H bond has the reverse polarity of C—H bond.

$$\overset{\delta+}{Si}—\overset{\delta-}{H} \qquad \overset{\delta-}{C}—\overset{\delta+}{H}$$

Silanes are reducing agents and are spontaneously inflammable. They are hydrolyzed by alkaline solutions to hydrous silica.

Halides : Group 14 elements form binary tetrahalides of the type MX_4 (except $PbBr_4$ and PbI_4). They are tetrahedral, covalent and susceptible to hydrolysis, although this tendency decreases as the basicity of the group 14 elements increases. Carbon tetrachloride is inert to water.

$$SiCl_4+4H_2O \longrightarrow Si(OH)_4+4HCl$$

Carbon tetrachloride is obtained by chlorination of CS_2. Both $SiCl_4$ and $GeCl_4$ are produced by heating the oxide and carbon in chlorine. Tin (IV) chloride is obtained by reaction of metal with chlorine. Lead (IV) chloride is obtained as an unstable yellow liquid by the reaction between PbO_2 and conc. HCl. Other tetrahalides are also obtained by the methods employed for tetrachlorides.

Silicon tetrafluoride (but not the other halides of Si) forms the complex hexafluoro ion $[SiF_6]^{2-}$. This is produced when SiF_4 is hydrolyzed.

$$SiF_4 + 2H_2O \longrightarrow SiO_2 + 4HF$$
$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

Other complex hexahalide ions are :

$[GeF_6]^{2-}$, $[SnF_6]^{2-}$, $[GeCl_6]^{2-}$, $[PbCl_6]^{2-}$, *etc.*

Germanium, tin and lead form dihalides. Generally they have greater ionic character in the solid state than the tetrahalides; for instance, their volatility is much less. Anhydrous Sn (IV) chloride is a fuming liquid, tin (II) chloride is a crystalline solid.

Tin (II) chloride can be prepared by boiling conc. HCl with tin or by action of HCl gas on heated tin. SnX_2 are mild reducing agents and they themselves get converted to SnX_4.Sn (II) reduces iron (III) to iron (II); mercury (II) to mercury (I) and then to mercury, permanganate to manganese (II) and dichromate to chromium (III) ions.

$$2HgCl_2 + Sn^{2+} \longrightarrow Sn^{4+} + Hg_2Cl_2(s) + 2Cl^-$$

If $SnCl_2$ is used in excess then $HgCl_2$ (or Hg_2Cl_2) is reduced to mercury.

$$Hg_2Cl_2(s) + Sn^{2+} \longrightarrow 2Hg(l) + Sn^{4+} + 2Cl^-$$

In basic solution Sn (II) acts as a stronger reducing agent than in acidic solution. Thus, the stannite ion is readily oxidized to the stannate ion, $[Sn(OH)_6]^{2-}$.

Lead (II) chloride, $PbCl_2$ can be prepared either by action of chlorine on lead or by reaction of chloride ions (HCl) on aqueous solution of lead ions. $PbCl_2$ is soluble is hot aqueous solution.

$$PbCl_2(s) + 2Cl^-(aq) \longrightarrow [PbCl_4]^{2-} (aq)$$

This reaction is the basis of its identification in qualitative analysis.

Silicates. The naturally occurring silicates are the most common rock-forming minerals. They are also of considerable commercial importance. Asbestos and micas are used as insulators, granite is a building stone, the various types of clays find uses in the manufacture of bricks, pottery and china, and minerals such as beryl, topaz and garnet are valued as gemstones.

The composition of the silicates is often variable as one metal is replaced by other metals. For example, many forms of olivine, Mg_2SiO_4 are known in which magnesium is replaced by iron or other metals.

Structurally, the silicates consist of metal cations and anions that consist of silicon atoms covalently and tetrahedrally bonded to four oxygen atoms. The basic difference among the various silicates lies in the structure of the anion. The anion can exist as discrete SiO_4^{4-} ion, as two SiO_4 tetrahedral linked through one oxygen atom, as tetrahedra linked through two or the oxygen of each tetrahedron or as tetrahedra linked through three of the oxygen atoms of each tetrahedron. They have been discussed in Unit 2.

Silicones. Silicones are polymeric organosilicon compounds containing individual or cross linked —Si—O—Si—O chains or rings in which some of the oxygens of SiO_4 tetrahedra are replaced by groups such as hydroxyl, —OH; methyl, CH_3; ethyl, C_2H_5; or phenyl, —C_6H_5. They exhibit some of the properties of hydrocarbons; and some of the properties of silicon oxygen compounds. Since the empirical formula is that of a ketone $(R_2CO)_x$ the name silicone has been given to these materials. They find many applications because of their remarkable stability to chemical attack or thermal decomposition.

Preparation of silicones involve three steps : (*i*) preparation of alkyl or aryl substituted halogen silanes, (*ii*) hydrolysis to organosilicon hydroxides known as silanols, and (*iii*) condensation of silanols to silicones by heating or by the action of acids.

(*i*) **First step :** Alkyl (or aryl) substituted halogen silanes can be prepared either by the reaction between alkyl (or aryl) halides and silicon in the presence of copper as catalyst (10% by mass) at about 600K or by the reaction between $SiCl_4$ and Grignard reagent (RMgCl).

$$\underset{\text{Methyl chloride}}{CH_3Cl+Si} \xrightarrow[\text{600K}]{\text{Cu-powder}} \underset{\text{Dimethyldichlorosilane}}{(CH_3)_2SiCl_2}$$

$$SiCl_4+RMgCl \longrightarrow RSiCl_3+MgCl_2$$

$$RSiCl_3+\underset{\text{Grignard reagent}}{RMgCl} \longrightarrow R_2SiCl_2+MgCl_2$$

The above reaction, thus, produces alkyl or arylchlorosilanes—($RSiX_3$, R_2SiX_2 and R_3SiX), SiR_4, SiX_4, $MeSiHX_2$, *etc.* (R=alkyl or aryl, X=chlorine).

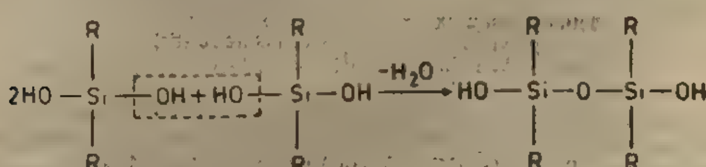
(*ii*) **Second step** : Hydrolysis of organochlorosilanes to silanols.

$$R_1SiCl_3+3H_2O \longrightarrow R_1Si(OH)_3+3HCl$$

$$R_2SiCl_2+2H_2O \longrightarrow R_2Si(OH)_2+2HCl$$

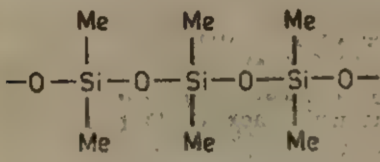
$$R_3SiCl+H_2O \longrightarrow R_3Si(OH)+HCl$$

(*iii*) **Third step.** Condensation of silanols to silicones by heating or by the action of acids :

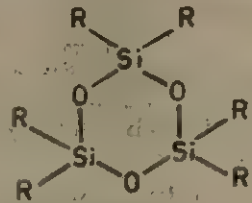


This arises from intermolecular condensation, with elimination of water.

Diols formed by hydrolysis of R_2—Si—Cl_2 can condense further under carefully controlled conditions to give chains or rings, *e.g.*,



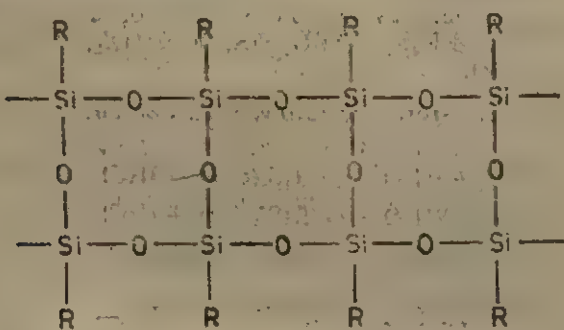
Poly-dimethyl siloxane
(silicone oil)
(chain silicone)



Cyclic dimethyl siloxane
(cyclic silicone)

A ring silicone may be converted into chain polymer by heating with H_2SO_4.

The presence of an active —OH group at each end of the chain helps in extending the length of the chain. The chain length is controlled by the proportion of R_3SiCl present for condensation. The presence of $RSiCl_3$ in the reactants produces cross-linked silicones since this generates a third Si-O function in addition to the two required for polymerization.



Methylsilsesquioxane ladder polymer (Cross linked silicone)

(Siloxanes)
(Silicone resins)

Liner siloxanes have also been made by hydrolyzing Me_2SiCl_2 in the presence of varying amounts of Me_3SiCl_2 as a chain stopping group, *i e.,* $[Me_3SiO\ (Me_2SiO)_x\ SiMe_3]$ (x=0, 1, 2, 3, 4, *etc.*).

The extent of cross-linking and the nature of the alkyl or aryl group determine the properties of silicones. The polymers range

from liquids to hard, thermally stable solids. Silicones are water repellent and thermally and electrically insulating. These properties lead to their extensive use in industries.

Other organometallic compounds. Apart from silicones there are many organocompounds of the group 14 elements. Tetraethyl lead, an important compound is a very poisonous liquid which is widely used as an antiknock in petrol. It is produced by heating a mixture of ethyl chloride and sodium-lead alloy.

10.7. GROUP 15 ELEMENTS : THE NITROGEN FAMILY

Group 15 of the periodic table contains nitrogen (N), phosphorous (P), arsenic (As), antimony (Sb) and bismuth (Bi). The elements show the usual trends within the group. The metallic character increases going down the group. Thus, N and P are non-metals, As and Sb are metalloids, and Bi is metallic. All the elements are characterized by $ns^2\ np^3$ electrons in their valence shell which would suggest the formation of -3, $+3$ and $+5$ oxidation states and these are observed in P, As, Sb and Bi. Nitrogen, however, is found in every oxidation state between -3 and $+5$. Further in this group nitrogen is a gas and rest of the members of the group are all solids. Ions with a charge of 3$-$occur only for nitrogen and phosphorus. All elements exhibit 3$-$*i.e.*, M^{3-} oxidation state in covalent compound such as NH_3, PH_3, ... BiH_3. There is a decrease in the strength of the covalent bonding in the sequence P$>$As$>$Sb$>$Bi. The heavier elements of this group (Sb and Bi) tend to lose their electrons to form M^{3+} cations, a tendency which is in accord with the decreasing ionization energy from nitrogen to bismuth (Table 10.9). When the elements are combined with highly electronegative elements it is possible to assign +ve oxidation states. These are usually $+3$ and $+5$, but for arsenic, antimony and bismuth the $+5$ state is often less stable than $+3$ state. Thus, the M^{5+} ion does not exist and the $+5$ oxidation state is realised only through covalent bonding. The $+5$ oxidation state is seen in covalent compounds like PF_5, H_3PO_4 and in polyatomic ions such as NO_3^-, PO_4^{3-}. M^{3+} cations probably exist for Sb and Bi in compounds like $Sb_2(SO_4)_3$, $Bi(ClO_4)_3 . 5H_2O$., *etc.*, although in aqueous solution they are extensively hydrolyzed to SbO^+X^- and BiO^+X^- (X^-=univalent anion) to give strong acidic solutions.

TABLE 10.9 : Some physical properties of group 15 elements

Property	*N*	*P*	*As*	*Sb*	*Bi*
Atomic number	7	15	33	51	83
Electronic configuration	$[He]2s^22p^3$	$[Ne]3s^23p^3$	$[Ar]3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$
Covalent radius,* r/pm (single bond)	70	110	120	140	150
Ionic radius, M^{3-}, $r_{M^{3-}}$/pm	171	212	222	—	—
M^{3+}, $r_{M^{3+}}$/pm	—	—	—	76	103
Ionization energy, IE/kJ mol^{-1} 1st	1402	1012	947	834	703
2nd	2856	1903	1798	1595	1610
3rd	4577	2910	2736	2443	2446
Electronegativity	3.0	3.1	2.0	1.9	1.9
Electron affinity/ kJ mol^{-1}	−31	60	—	—	—
Melting point, T/K	63.2	316 (white)	1089 (Grey α-form)	903.7	544.4
Boiling point, T/K	77.2	553 (white)	888 (sublime)	1860	1837
Density at 298K, ρ/g cm^{-3}	0.88 (63 K)	1.82	5.78 (grey α-form)	6.7	9.81
Oxidation state	−3, −2, −1, +1, +2, +3, +4, +5	−3, +1, +3, +5	−3, +3, +5	+3, +5	+3, +5

As seen in other groups, nitrogen differs in many respects from the other members of the group. The factors like small size, high electronegativity and absence of d orbitals are responsible for its unique nature. Nitrogen displays a great tendency to form $p_\pi - p_\pi$ multiple bonds (like in azo group, $-N=N-$; in cyanide ion, $-C\equiv N$; in nitro group, $-\mathrm{N}\begin{array}{l} \diagup \mathrm{O} \\ \diagdown \mathrm{O} \end{array}$; *etc.*) with itself as well as with carbon and oxygen. For the heavier members of the group, the relative strengths of double and triple bonds relative to single bond diminish markedly.

The elemental nitrogen exists as the multiple bonded stable molecule $N\equiv N$, whereas phosphorus exists as solid in various forms containing single bonded phosphorus. This is because the bond energy (BE) of $N\equiv N$ is much greater than triple bonded phosphorus *i.e.*, $BE_{P-P} > BE_{P\equiv P}$, but the reverse is true for single bonds, $BE_{N\equiv N} > BE_{N-N}$.

Phosphorus shows a distinct tendency for catenation forming both cyclic and open chain compounds containing several phosphorus atoms. Nitrogen, as compared to phosphorus, shows a poor

tendency for catenation because of the relative weakness of the N−N single bond compared to the single P—P bond ($BE_{P-P} > BE_{N-N}$). Compounds containing N−N bonds are unstable with respect to decomposition into the elements, and also to oxidation. Hydrazine, *e.g.*, NH_2—NH_2 decomposes into NH_3, N_2 and H_2 at 523 K. In general the catenation tendency decreases in order P>N>As >Sb>Bi.

Nitrogen forms compounds with a maximum covalency of four (NH_4^+, NR_4^+) because only four orbitals are available for bonding (nitrogen has no d orbitals in its valence shell). The havier elements all have vacant d orbitals which can be used in bonding and show an extra valency of 5 and a maximum covalency of six, *e.g.*, PCl_5, AsF_5, PF_6^-, *etc.* Phosphorus and the heavier members of the family do not readily form $p_\pi - p_\pi$ multiple bonds whereas many compounds are known where multiple bonding of the $d_\pi - p_\pi$ type exist. The latter type of bonding is particularly prominent for phosphorus as reflected in the formation of compounds such as $O{=}PX_3$, $RN{=}PX_3$, $O{=}PH(OH)_2$, $O{=}P(OH)_3$, and $(N{=}PCl_2)_n$. Nitrogen takes part in hydrogen bonding. The difference in the physical properties of NH_3 and PH_3 is due to hydrogen bonding. Oxides of nitrogen are small molecules, whereas oxides of phosphorus are solid and polymeric substances with single P—O bonds. This is because nitrogen can form multiple bonds to oxygen. Molecular nitrogen is unusually inert because of its high bond dissociation energy (946 kJ mol^{-1}). Nitrogen forms numerous compounds with sp and sp^2 hybridizations. Such hybridizations are not seen in the compounds formed with P.

Phosphorus atoms unite into diatomic P_2, tetratomic P_4 and polymeric P_n molecules. P_2 molecules have a structure similar to that of N_2 and exist only above 1073 K. In the liquid or vapour from, P_4 molecules are stable below 1073 K. Thus, the most stable form is P_4. Both arsenic and antimony exists as tetrahedral molecules in their elemental state.

Phosphorus exists in several allotropic forms of which only three are important. These are white or yellow, red and black phosphorus. White phosphorus exists as P_4 molecules (tetrahedral). Red phosphorus has a polymeric type of structure resulting from the partial breakdown and interlinking of P_4 tetrahedral units to give P_n (Fig. 10.16). Black phosphorus (also P_n) possesses graphite-like structure, but the layers are corrugated rather than planar, each P atom being bound to three neighbours.

Arsenic, antimony and bismuth also exist in several allotropic modifications ; the most stable forms at room temperature have structures similar to that of black phosphorus.

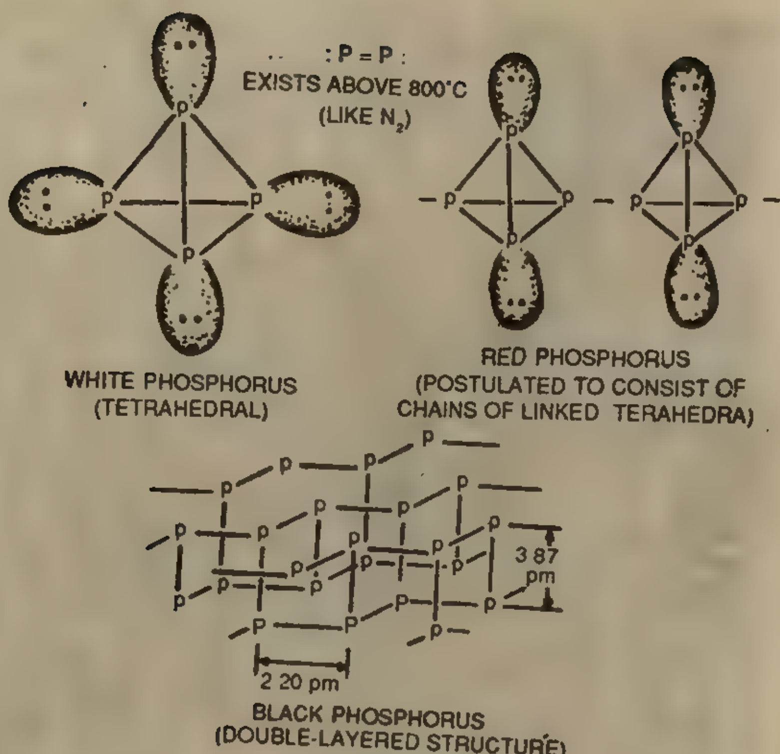


Fig. 10.16. Arrangement of atoms in the different allotropic forms of phosphorus.

10.7.1. Chemical Properties of Group 15 Elements and their Trends

Nitrogen is almost unreactive at room temperature. The only exception is the reaction with metallic lithium to form the nitride

$$Li\ (s) + N_2(g) \longrightarrow 2Li_3N\ (s)$$

and fixation of nitrogen by some bacteria. It reacts with O_2 and hydrogen only at high temperatures yielding NO and NH_3 respectively. Other elements in the group also react with oxygen. White phosphorus combines with oxygen so readily that it is necessary to store the element under water to prevent it igniting. The products of reaction are P_4O_6 ond P_4O_{10}. The other elements in the group yield the trioxide only. Combination of the group 15 elements (except nitrogen) with other non-metals, *e g.*, the halogens and sulphur, occurs readily. All react with some metals, but the products differ : nitrogen forms ionic and interstitial nitrides. whereas others form phosphides, arsenides, *etc.* which are not interstitial.

10.7.2 Compounds of Group 15 Elements

Oxides. The important oxides of group 15 elements are listed in Table 10·10 along with their methods of preparation. Nitrogen assumes only positive oxidation states with oxygen because oxygen is more electronegative than nitrogen. The ability of nitrogen to form multiple bonds to oxygen causes its oxides to be small molecules, not solid polymeric substances with simple M—O bonds as in the case of P, As, *etc.* Nitrogen-oxygen chemistry is rather complex. We shall here present a mere outline to give the students a feeling for the behaviour of the nitrogen atom in different environments. Their structures are given in Fig. 10.17. Dinitrogen oxide, N_2O and nitrogen oxide, NO are neutral, and for other oxides acidity increases $N_2O_3 < NO_2 < N_2O_5$.

Both nitrogen monoxide and nitrogen dioxide are used in the manufacture of nitric acid. Dinitrogen tetraoxide has found its use as an oxidant for rocket fuels in missiles and space vehicles. Dinitrogen oxide is used for anaesthetic purposes. Nitric oxide is one of the atmospheric pollutants emitted during the burning of oil and coal (in power stations, refineries and automobiles).

Oxides corresponding to oxidation states +3 and +5 are the two principal oxides of phosphorus, P_4O_6 and P_4O_{10}, obtained when phosphorus is burnt in air (O_2). The lower oxide is obtained in a limited supply of air. Both P_4O_6 and P_4O_{10} are the acid anhydrides of H_3PO_3 and H_3PO_4 respectively. Thus the, oxides on hydrolysis give their corresponding oxyacids.

$$P_4O_6 + 6H_2O \longrightarrow \underset{\text{Phosphorous acid}}{4H_3PO_3}$$

$$P_4O_{10} + 2H_2O \longrightarrow \underset{\text{Metaphosphoric acid}}{4HPO_3}$$

$$2HPO_3 + H_2O \longrightarrow \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7}$$

$$H_4P_2O_7 + H_2O \longrightarrow \underset{\text{Phosphoric acid}}{H_3PO_4}$$

The structure of these oxides is based on a tetrahedral arrangement of four phosphorus atoms. These phosphorus atoms are linked by six bridging oxygen atoms in the case of P_4O_6. But in the case of P_4O_{10}, in addition to six bridging oxygen atoms, each phosphorus atom is attached to a fourth oxygen atom which is directed away from the P_4 tetrahedron (Fig. 10.18). The disposition of oxygen atoms around each phosphorus atom is thus tetrahedral.

Phosphorus pentoxide has strong affinity for water ; it even removes the elements of water from conc. H_2SO_4. Thus, it serves as a good dehydrating agent.

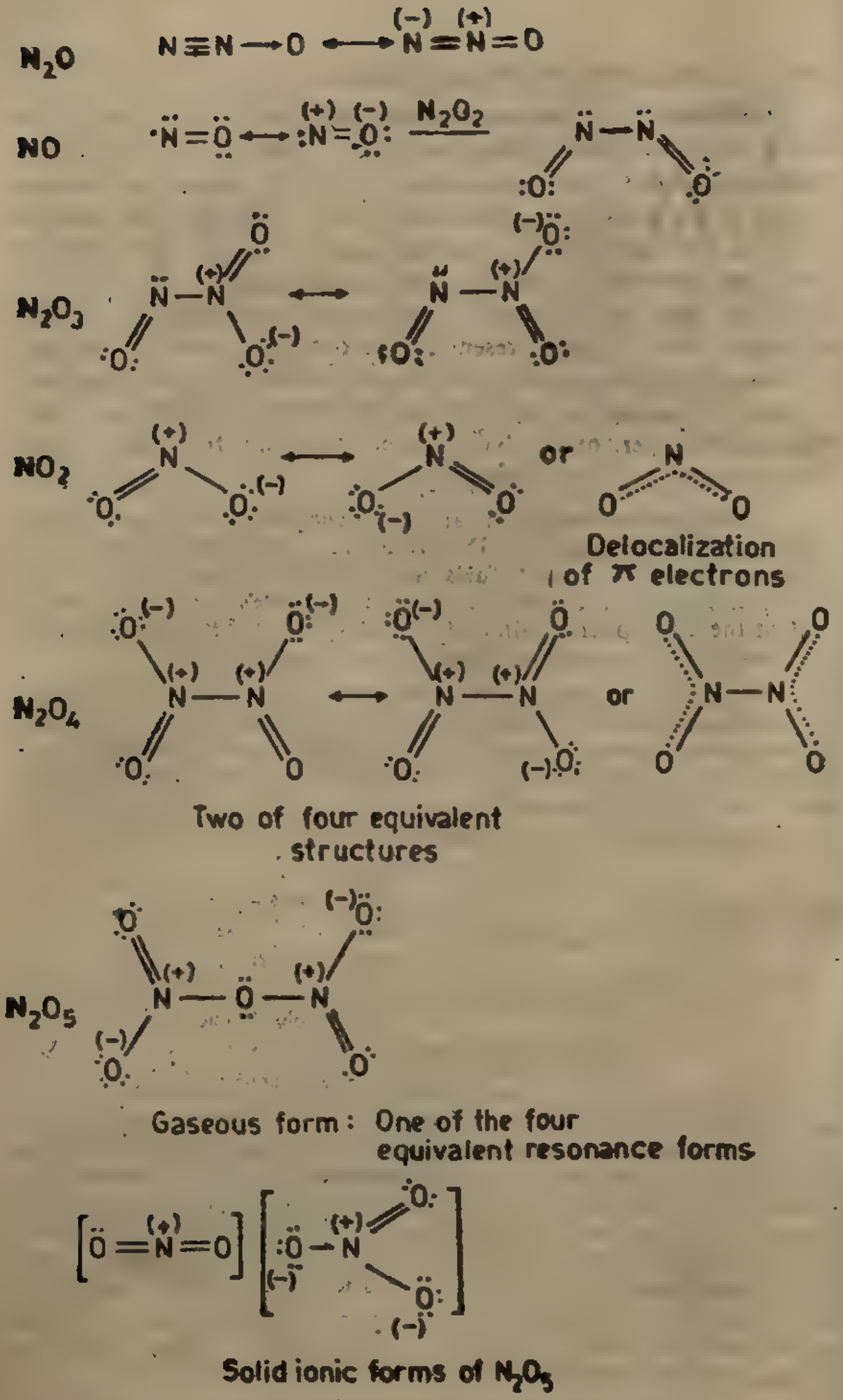
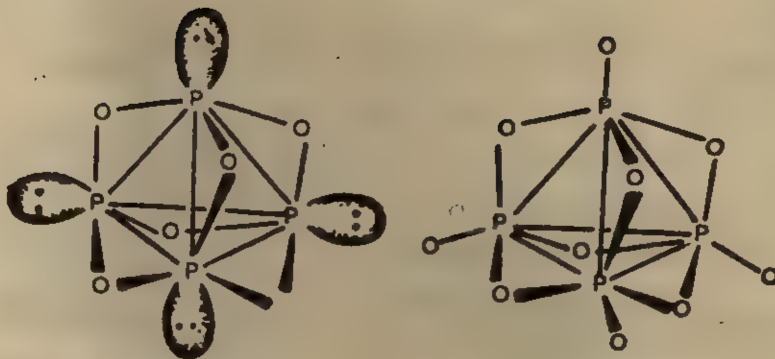


Fig. 10.17. Structures of the oxides of nitrogen



(a) P_4O_6 (b) P_4O_{10}

TETRAHEDRON OF OXYGENS ABOUT EACH PHOSPHORUS

Fig. 10.18. Structures of (a) P_4O_6) and P_4O_{10}

TABLE 10.10 : Group V oxides

Oxide	*Preparation*	*Comments*
N_2O	$NH_4NO_3(s) \xrightarrow[443\ K]{Heat} N_2O(g)+2H_2O(g)$	Neutral, rather inert ; mild anaesthetic
NO	$3Cu+$Dil. $8HNO_3 \longrightarrow 3Cu(NO_3)_2+4H_2O+2NO$ $6NaNO_2+$Dil. $3H_2SO_4 \longrightarrow 4NO+2H_2O+3Na_2SO_4+2HNO_3$ **Industrial preparation** $4NH_3+5O_2 \xrightarrow[Catalyst]{Rh\text{-}Pt} 4NO+6H_2O$	Neutral, reactive, odd-electron compound ; forms NO^+ readily. Readily oxidized, $2NO+O_2 \longrightarrow 2NO_2$. Dimeric in solid and liquid state. Forms nitrosyl complexes with transition metals.
$NO_2 \rightleftharpoons N_2O_4$	$Cu+$Conc. $4HNO_3 \longrightarrow 2NO_2+Cu(NO_3)_2+2H_2O$	Acidic, reactive, odd-electron compound. Bent molecule. Forms NO_2^+ (linear) and NO_2^- (more bent).
$NO_2 \rightleftharpoons N_2O_4$	$2Pb(NO_3)_2 \longrightarrow 4NO_2+2PbO+O_2$	Decomposes above 873 K to NO and O_2. N_2O_4 exists in several forms in solid state. Most stable form is planar with an unusually long N—N bond. NO_2 a brown gas, whereas N_2O_4 a colourless gas. N_2O_4 is available in liquid form.
N_2O_3	$4HNO_3+As_4O_6+4H_2O \longrightarrow 4H_3AsO_4+2N_2O_3$	Blue solid ; decomposes above 253 K to NO and NO_2.

Oxide	Preparation	Comments
	$4NO+O_2 \longrightarrow 2N_2O_3$	Planar molecule with a very long N—N bond.
	$2NO+N_2O_4 \longrightarrow 2N_2O_3$	With alkali gives NO_2^- ion (nitrite).
N_2O_5	$4HNO_3+P_4O_{10} \longrightarrow 2N_2O_5+4HPO_3$	Planar molecule O_2N—O—NO_2 in gas (Fig. 10.17).
	$2NO_2+N_2O_4 \longrightarrow 2N_2O_5$	In solid exists as NO_2^+, NO_3^-. Reacts with water to give HNO_3.
P_4O_6	$P_4+3O_2 \longrightarrow P_4O_6$ (limited supply of O_2)	Structure given in Fig. 10.18. Reacts with water to give H_3PO_3. Reacts wirh halogen X_2 to give POX_3.
P_4O_{10}	$P_4+5O_2 \longrightarrow P_4O_{10}$	Structure given in Fig. 10.18. Very powerful drying agent, reacts with water to give H_3PO_4 (intermediate products are HPO_3 and $H_4P_2O_7$).
As_4O_6	$As_4+3O_2 \longrightarrow As_4O_6$ (limited supply of O_2)	Amphoteric oxide, slightly soluble in water. Same structure as P_4O_6 in gaseous state.
As_2O_5	$As_4O_6+HNO_3 \longrightarrow H_3AsO_4.H_2O \xrightarrow[443\ K]{Heat} As_2O_5$	Structure unknown ; acts as an oxidizing agent, in water gives H_3AsO_4.
Sb_4O_6	$Sb_4+3O_2 \xrightarrow{Heat} Sb_4O_6$	Amphoteric, same structure as P_4O_6.
Sb_2O_5	$Sb+HNO_3 \xrightarrow{Heat} Sb_2O_5$	Structure unknown.
	$SbCl_5+OH^- \xrightarrow{Heat} Sb_2O_5$	
Bi_2O_3	By heating $Bi(OH)_3$ or $Bi(NO_3)_3$	Soluble in acids, but not in alkali.
Bi_2O_5	Bi_2O_3+strong oxidizing agent $\longrightarrow Bi_2O_5$	Loses O_2 thermally. Oxidizing agent.

Oxo-acids. The most important oxo-acid of nitrogen is nitric acid (Unit 12, Class XI textbook). Two other important oxo-acids of nitrogen are nitrous and hyponitrous acids. Hyponitrous acid ($H_2N_2O_2$) is a weak dibasic acid and has the structure, HON=NOH.

Although nitrous acid is unstable, and cannot be isolated in pure form, N_2O_3 can be considered its anhydride. The reaction of N_2O_3 with aqueous alkali produces nitrite salts.

$$N_2O_3+2\,[Na^++OH^-] \longrightarrow 2\,[Na^++NO_2^-]+H_2O$$

The acid is obtained when H_2SO_4 reacts with cold aqueous solution of nitrite. It is a weak acid and acts both as an oxidizing and reducing agent.

It is an important component for diazotization in dye industry.

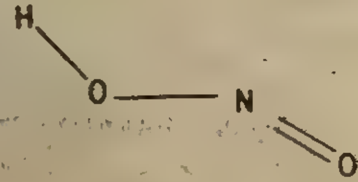


Fig. 10.19. Nitrous acid, HNO_2.

Nitric acid is commercially prepared by the Ostwald process. At high temperatures, NH_3 is catalytically oxidized to NO, which is cooled and, in turn, oxidized to NO_2. Nitrogen dioxide on reacting with water gives HNO_3.

$$4NH_3+5O_2 \xrightarrow[1273\,K]{Pt} 4NO\,(g)+6H_2O\,(g)$$

$$2NO+O_2 \longrightarrow 2NO_2\,(g)$$

$$3NO_2+H_2O \longrightarrow 2\,[H^++NO_3^-]+NO\,(g)$$

Pure HNO_3 is colourless and highly soluble in water. It is a strong acid. Light or heat causes it to decompose into NO_2, O_2 and H_2O. The presence of NO_2 is responsible for its *y*ellow colour.

Nitric acid is a strong oxidizing agent when concentrated. Its reduction products vary greatly depending upon the reducing agent and the concentrations involved, e.g.,

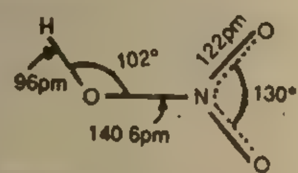


Fig. 10.20. Nitric acid, $HNO_3\,(g)$.

$$Cu+2NO_3^-+4H^+ \longrightarrow Cu^{2+}+2NO_2+2H_2O$$

$$3Cu+2NO_3^-+8H^+ \longrightarrow 3Cu^{2+}+2NO+4H_2O$$

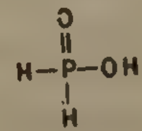
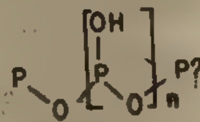
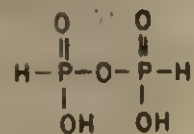
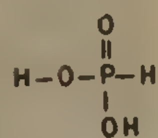
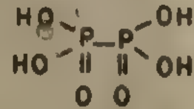
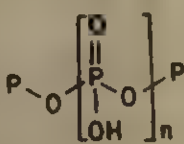
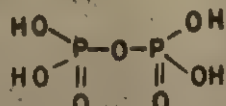
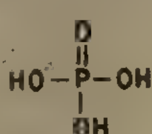
$$4Zn+2NO_3^-+10H^+ \longrightarrow 4Zn^{2+}+N_2O+5H_2O$$

$$4Zn+NO_3^-+10H^+ \longrightarrow 4Zn^{2+}+NH_4^++3H_2O$$

It dissolves nearly all metals. It is used (*i*) in the manufacture of fertilizers, explosives, dyes, plastics, synthetic fibres, *etc*., (*ii*) in the extraction of certain metals, (*iii*) in the manufacture of different nitrates and chemicals, and (*iv*) as a laboratory reagent.

Phosphorus forms numerous oxo-acids (Table 10.11), all of which are based on a tetrahedral four-coordinated phosphorus containing at least one P=O unit and one P—OH group.

Table 10.11 : Oxyacids of phosphorus

Oxidation state of phosphorus	*Acid*	*Name*	*Preparation*	*Structure*
+1	H_3PO_2	Hypophosphorous	P_4 + Alkali → $H_2PO_2^- + H_2$	
+3	$(HPO_2)_n$	Metaphosphorus		
	$H_4P_2O_5$	Pyrophosphorous	$PCl_3 + H_3PO_3$	
	H_3PO_3	Orthophosphorous	P_4O_6 or PCl_3 $+ H_2O$	
+4	$H_4P_2O_6$	Hypophosphoric	Red P + Alkali	
+5	$(HPO_3)_n$	Metaphosphoric	By heating orthophosphoric acid	
	$H_4P_2O_7$	Pyrophosphoric	By heating phosphates	
	H_3PO_4	Orthophosphoric	$P_4O_{10} + H_2O$	

The most highly hydroxylated acid known in a particular oxidation state is the ortho acid. The meta acid is obtained by the loss of one molecule of water from the ortho acid and the pyro acid is the intermediate produced by the action of heat and loss of a water molecule from two molecules of ortho acids. The prefix, 'hypo' generally shows a lower oxygen content than the parent acid. The oxyacids of phosphorus contain acidic hydrogens bonded to oxygen

$$\rangle P-O-H \rightleftharpoons P-O^- + H_3^+O$$

or non-acidic hydrogen atoms linked directly to phosphorous atom, $\rangle P-H$.

In the case of orthophosphoric acid all the hydrogens are acidic, and hence, can be ionized.

Orthophosphoric acid is a major industrial chemical. It is manufactured either by treating rock phosphate (or bone ash) with conc. H_2SO_4 or by hydrating phosphorus pentoxide.

The pure acid is a three-dimensional hydrogen bonded structure. It is often sold as an 85% solution in water called 'syrupy phosphoric acid'. The high viscosity of this solution arises from intermolecular hydrogen bonding. It is a relatively weak triprotic (or tribasic) acid, the successive ionization constants (expressed in terms of pK units) being 2.12, 7.2 and 12.4 at 298 K.

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$$

$$H_2PO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$$

It forms three types of salts, *e g*., NaH_2PO_4, Na_2HPO_4 and Na_3PO_4. Most phosphates are insoluble in water.

In the discussion of the oxyacids you have come across, —P—P— and —P—O—P— linkages. Condensed acids containing —P—P— bonds are more slowly hydrolyzed than those containing P—O—P bonds. The —P—O—P— linkages are of great biochemical importance. Certain biologically active molecules on which all life depends, *e.g*., aderosine triphosphate (ATP) contains this linkage. This phosphate ester plays a vital role in life processes such as, protein synthesis, genetic coding, photosynthesis, nitrogen fixation and many other metabolic pathways. Hydrolysis of this ester releases the energy required for many biochemical processes. Thus phosphate groups are called "high energy phosphate".

The other important biomolecules which contain phosphate groups are DNA, RNA, adenosine, mono-, di- and tri-phosphates (AMP, ADP and ATP) (Units 16 and 17).

Alkali and alkaline earth phosphates are widely used in the manufacture of detergents. Certain phosphates are also used as fertilizers, water softeners and in the manufacture of plasticizers and insecticides.

Hydrides. All elements of group 15 form hydrides of the general formula MH_3 of which ammonia (NH_3) is the most important (Unit 12, Class XI textbook). Industrially ammonia is made directly from its elements by the Haber process. Phosphine (PH_3), like ammonia is obtained from the hydrolysis of ionic phosphides.

$$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$$

as well as by the reaction of concentrated base on white phosphorous.

$$P_4 + 3KOH + 3H_2O \longrightarrow PH_3 + 3KH_2PO_4$$

Arzsine, AsH_3, can be obtained by hydrolyzing a metal arsenide or by reducing an acidified solution of arsenic.

The hydrides SbH_3 (stibine) and BiH_3 (bismuthine) can be produced in small amounts by methods similar to those used for arsine.

$$Zn_3M_2\,(s) + 6HCl\,(aq) \longrightarrow 2MH_3\,(g) + 3ZnCl_2\,(aq)$$
$$(M = As,\ Sb \text{ or } Bi)$$

$$H_3AsO_3\,(aq) + 3Zn\,(s) + 6H^+\,(aq) \rightarrow AsH_3 + 3Zn^{2+}\,(aq) + 3H_2O\,(1)$$

All the group 15 hydrides except ammonia are toxic. The stability of these hydrides decreases sharply from NH_3 to BiH_3 as is shown by the average bond energies (Table 10.12). AsH_3, SbH_3 and BiH_3 are increasingly thermally unstable and have strong reducing properties. They have a lone pair of electrons attached to the central atom, and hence, the potentiality of behaving as Lewis bases. The strength of each species as a Lewis base decreases as the group is descended. Ammonia is the strongest base and is thus the most soluble in water. It forms hydrogen bonds with water.

$$\underset{\text{Base}}{H_3N:} + \underset{\text{Acid}}{H{-}OH} \longrightarrow H_3NH^+ \cdots\cdots OH^-$$

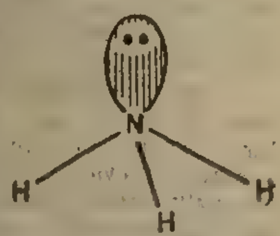
This type of acid-base interaction, with other hydride, is reduced considerably and the solubility in water is negligible. Hydrides other than NH_3 are not associated in liquid state through hydrogen bonding. Because of hydrogen bonding in ammonia, the hydride shows exceptionally high melting and boiling points compared to the other hydrides of the group (Table 10.12).

TABLE 10.12 : Properties of hydrides of group 15 elements

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point, T/K	195.2	139.5	156.7	185	—
Boiling point T/K	238.5	185.5	210.6	254.6	290
(M—H) distance/pm	101.7	141.9	151.9	170.7	—
Bond angle, HMH	106°.45′	93°.6′	91°.8′	91°.3′	—
ΔH_f/kJ mol^{-1}	−46.1	13.4	66.4	145.1	278
Bond energy, BE(M—H)/kJ mol^{-1}	391	322	247	255	—

The ammonia molecule is pyramidal with an H—N—H bond angle 106°45′. A decrease in bond angle is observed (Table 10.12) from NH_3 to SbH_3. This decrease is associated with a decrease in the electronegativity of the central atom.

Related nitrogen hydrides are hydrazine, NH_2—NH_2 and hydroxylamine, NH_2OH, in which an N—H bond of NH_3 is replaced by N—N and N—O bonds respectively. Hydrazine is made by oxidizing aqueous ammonia with sodium hypochlorite in the presence of a little glue (the Raschig process).



NH$_3$ molecule

Fig. 10.21. Ammonia, NH_3.

$$NH_3+NaOCl \longrightarrow NH_2Cl+NaOH$$
$$NH_2Cl+NH_3+NaOH \longrightarrow N_2H_4+NaCl+H_2O$$

It is a powerful reducing agent. It is a reasonably stable liquid although its heat of formation is positive (+50 kJ mol^{-1}). However, its combustion is highly exothermic.

$$N_2H_4\,(l)+O_2\,(g) \longrightarrow N_2\,(g)+2H_2O\,(l)$$
$$(\Delta H=-622 \text{ kJ mol}^{-1})$$

which has led to its use as a fuel in rockets and fuel cells.

In the preparation of PH_3, some diphosphine, P_2H_4 is also formed. It is a strong reducing agent and is analogous to hydrazine in most properties.

Halides. Two series of compounds, the tri- and pentahalides are known for phosphorus and the heavier elements (Table 10.13). Trihalides only are formed by nitrogen because its maximum covalency is four.

TABLE 10.13 : Halides of group 15 elements

MX_3 series	NF_3	NCl_3	NBr_3	NI_3
	PF_3	PCl_3	PBr_3	PI_3
	AsF_3	$AsCl_3$	$AsBr_3$	AsI_3
	SbF_3	$SbCl_3$	$SbBr_3$	SbI_3
	BiF_3	$BiCl_3$	$BiBr_3$	BiI_3
MX_5 series	PF_5	PCl_5	PBr_5	PI_5
	AsF_5	$AsCl_5$		
	SbF_5	$SbCl_5$		
	BiF_5			

All the possible trihalides have been prepared either as pure compounds or as ammonia adducts. They are generally prepared either by heating an excess of the element in the appropriate halogen or by the action of the concentrated hydrohalic acids on the oxide. NF_3 is, however, prepared by the electrolysis of anhydrous ammonium bifluoride, NH_4HF_2.

Nitrogen trifluoride is an inert (unreactive) gas, which is insoluble in water and does not hydrolyse. NCl_3 is a highly reactive liquid which is easily hydrolyzed. It is a very unstable molecule and explodes violently when warmed. Both NBr_3 and NI_3 are also thermally unstable, and are isolated as ammonia adducts $NBr_3.6H_2O$ and $NI_3.nH_2O$ (n=1 to 12).

The binary compounds, with the exception of the ionic BiF_3 (*mp* 1000 K), are all covalent molecular substances. Their structures are pyramidal. The shape arises from a tetrahderal arrangement of three bonding and one non-bonding pairs of electrons around the central atom. Of all the trihalides, PCl_3 is the most important. On hydrolysis, PCl_3 yields HCl and H_3PO_3

$$PCl_3+3H_2O \rightarrow 3HCl+H_3PO_3$$

but with NCl_3 the products are NH_3 and HOCl.

$$NCl_3+3H_2O \rightarrow NH_3+3HOCl$$

$AsCl_3$ is also hydrolyzed to AsH_3 and H_3AsO_3. Antimony and bismuth are more basic elements and hydrolysis of their chlorides can be suppressed by adding acid. They produce insoluble compounds containing oxychlorides SbOCl and BiOCl.

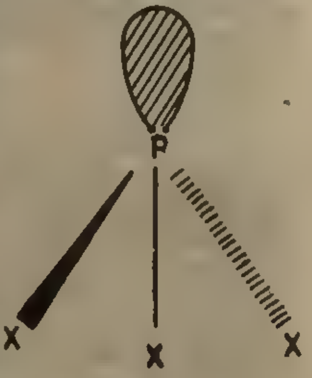


Fig. 10.22. Pyramidal molecule of PX_3.

The stability of the pentahalides decreases down the group and on going from fluoride to iodide. Phosphorus pentachloride is the best known of the pentahalides. It is produced by the reaction of chlorine on PCl_3. It is hydrolyzed to $POCl_3$ and then to H_3PO_4.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

PCl_5 is an industrial intermediate for various phosphorus compounds. The pentahalides are trigonal bipyramidal molecules in the gaseous state and the central atom is accordingly sp^3d hybridized. Solid PCl_5 has an ionic lattice containing $[PCl_4]^+$ and $[PCl_6]^-$ ions.

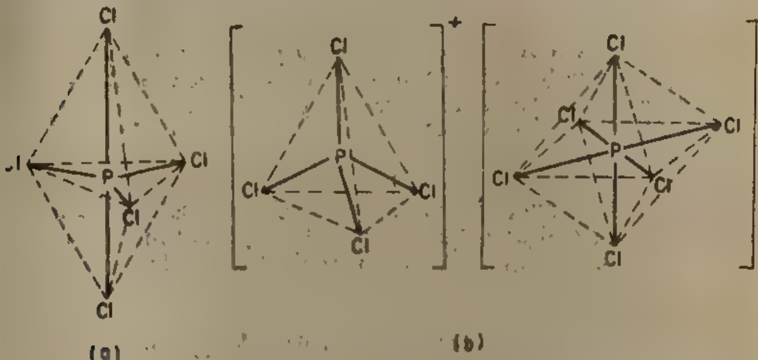


Fig. 10 23. Structures of (a) gaseous PCl_5, and (b) solid PCl_5

In solid PBr_5 the corresponding anion, $[PBr_6]^-$ does not exist because of the difficulty of accommodating six bromine atoms around the phosphorus atom.

10.8. GROUP 16 ELEMENTS : THE CHALCOGENS

Group 16 of the periodic table consists of five elements—oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). The first four elements are called chalcogens (means : ore forming) because many metals are found as oxides and, sulphides and a few as selenides and tellurides in nature. Polonium is radioactive and derives its name from Poland, the home country of Marie Curie who discovered the element in 1898. There is a transition from non-metallic to metallic character going down the group. Both oxygen and sulphur are entirely non-metallic whereas from selenium onwards there is increasing metallic character as supported by the tendency of the heavier elements to form complex anions such as $SeBr_6^{2-}$, $TeBr_6^{2-}$, *etc.*

The chalcogens have the $ns^2\ np^4$ electron configuration and all show tendency to gain or share the two additional electrons in many of their compounds to form either a 2- ion (O^{2-}, S^{2-}) two covalent bonds (H—O—H, Cl—Se—Cl), or a 1- ion with one covalent bond (OH^-, SH^-). With oxygen, a few exceptions are seen in which the oxidation state is -1 (H_2O_2), $-\frac{1}{2}$(KO_2) or $+2$ (OF_2). The other three heavier elements are less electronegative and show formal positive oxidation state $+2$ (SF_2, $TeBr_2$, *etc.*), $+4$ (SO_2, SF_4, *etc.*)

and +6 (SO_3, SF_6, TeO_3, *etc.*). Furthermore, S, Se and Te have vacant d orbitals (absent with oxygen), which are used to form six bonds, *e.g.*, SF_6, $Te(OH)_6$, SeF_6, *etc.*

As discussed above, the tendency to accept a pair of electrons (donated by another atom) diminishes as the group is descended. With oxygen, this behaviour is seen in the amine and phosphine oxides, $R_3N \rightarrow O$ and $R_3P \rightarrow O$ respectively. In aqueous solution, alkali metal sulphides react with sulphur producing polysulphide ions, S_n^{2-}. This could be possible because of the donation of an electron pair from S_2^{2-} to an S atom. Polyselenides and polytellurides have also been obtained in this way.

Oxygen can bond to a maximum of four atoms, *e.g.*, basic beryllium acetate $Be_4O(CH_3COO)_6$ (Fig. 10.5). In H^+_3O, oxygen has a covalency of 3; oxygen atom forms two covalent bonds with the hydrogen atoms and uses a lone pair for coordination of the proton (H^+). S, Se, and Te can form upto 6 covalent bonds by the expansion of the valence shell to include d orbitals, as stated earlier. Group 16 elements have a tendency to form double bonds with other atoms like C, N and O. This tendency to form multiple bonds with other atoms decreases as we descend the group from sulphur to tellurium. This S=C=S is moderately stable ; Se=C=Se decomposes readily whereas Te=C=Te is unknown. This tendency is also seen in the properties and different structures of their oxides (Section 10.8.2).

As with nitrogen, catenation with oxygen occurs only to a very limited extent. Peroxides and superoxides contain two consecutive oxygen atoms. Sulphur has a strong tendency to catenation and there are many sulphur compounds which have no analogy elsewhere in the group, *e.g.*, polysulphur dichlorides, S_nCl_2 (n=3 to 6), compounds containing polysulphide ion, S_n^{2-}, sulphanes, H—S_n—H, the polythionic acids, $HO_3SS_nSO_3H$ and their salts and various allotropic forms of the element containing different-sized S_n rings and chains. The S—S bond is important in biological systems and is found in compounds such as cysteine (amino acid), some proteins and enzymes. This phenomenon of catenation decreases markedly going down the group. Both Se and Te form rings (Se only) and long chains in their elemental forms.

The strong tendency of catenation in sulphur is evident by the fairly high bond dissociation energy (bond energy) of S—S single bond (Table 10.14).

Oxygen forms a stable diatomic molecule (paramagnetic) while S, Se, Te and Po have more polyatomic molecules. This accounts for oxygen being a gas and the others being solid at room temperature. Both S and Se at room temperature are known to be composed of molecules containing eight atoms in a puckered ring like structure (Fig 10.24).

(a) (b)

Fig. 10.24. Structure of (a) O_2, and (b) S_8 molecules

The characteristics and general trends in properties are summarized in Table 10.14.

TABLE 10.14 : Properties of the oxygen group elements

Property	*O*	*S*	*Se*	*Te*	*Po*
Atomic number	8	16	34	52	84
Electron structure	[He] $2s^2 2p^4$	[Ne] $3s^2 3p^4$	[Ar] $3d^{10} 4s^2 4p^4$	[Kr] $4d^{10} 5s^2 5p^4$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$
Covalent radius					
Double bond, r/pm	62	94	107	127	—
Single bond, r/pm	74	104	117	137	168
Ionic radius, M^{2-}, $r_{M^{2-}}$/pm	140	184	198	221	230 (approximate)
Electronegativity	3.5	2.45	1.5	2.1	2.0
Electron affinity M^{-}	700	—330	—406	—	—
kJ mol^{-1}, M^{2-}	141	196	—	—	—
Ionization energy IE/kJ mol^{-1} 1st	1314	1000	941	869	813
Density at 293 K, ρ/g cm^{-3}	1.14 (at mp)	2.07 (Rhombic)	4.79	6.25	—
Melting point, T/K	55	392 (Monoclinic)	490	723	520
Boiling point, T/K	90	717.6	957.8	1663	1235
Oxidation states	—2	—2, +2 +4, +6	—2, +2 +4, +6	—2, +2, +4, +6	+2, +4
Abundance (ppm)	4660000	520	0.09	0.002	Trace
Bond energy, M-M BE/kJ mol^{-1}	395	214	184.8	138.6	—

Density, melting and boiling points and covalent (atomic) and ionic radii show a regular increase from oxygen to polonium. The

large difference in melting the boiling points between oxygen and sulphur can be accounted from their allotropic forms. These elements are characterized by high ionization potentials (Table 10.14), decreasing gradually from oxygen to polonium. High values indicate the reluctance of these elements to form the cations. Their electronegativities decrease with increasing atomic number. Thus, in view of the fall in electronegativity, metallic character within the group increases with increasing atomic size. As the electronegativity decreases the strength of the elements as oxidizing agents decreases. The electrode potential values also confirm the trend. Oxygen is a strong oxidizing agent. Oxygen, because of its small size, high electronegativity and non-availability of d orbitals assumes a distinct place in group 16.

Allotropy

Oxygen has two allotropes, *i.e.*, dioxygen (O_2) and ozone (O_3). Dioxygen is the usual and most abundant form of oxygen. It has a special significance for life on earth. Ozone is mainly present in the upper part of the atmosphere. It is formed by the action of ultraviolet rays on dioxygen. It exists as triatomic molecules.

Sulphur can exist in several allotropic forms. There are perhaps over a dozen different sulphur allotropes. The most common of the well-characterized sulphur allotropes are the orthorhombic and monoclinic forms (solid sulphur). Both contain covalently bound S_8 puckered rings, the difference in the allotropes being a difference in the crystal packing of the S_8 units (Fig. 10.25). Orthorhombic sulphur, the most stable form at ordinary temperature, changes to the monoclinic above 369 K. However, the inter-conversion between the two forms is slow depending upon the temperature. This kind of allotropy is described as enantiotropic (moving in both directions). These two forms are soluble in non-polar solvents such as benzene, carbon disulphide, ether and alcohol.

Catena sulphur. A third unstable but important allotrope is called plastic sulphur. This is an amorphous solid obtained from a supercooled liquid. This is a sticky elastic substance which can be drawn into long threads. It contains long helical chains of sulphur atoms (Fig. 10.25). It is insoluble in non-polar solvents. After a few days the long chains slowly disintegrate and reform the small

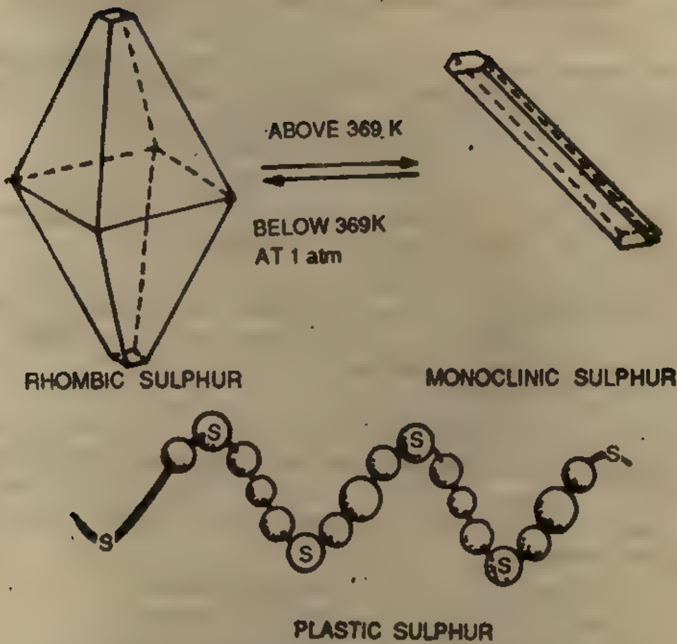


Fig. 10.25. Allotropes of sulphur

S_8 rings which crystallise gradually in rhombic lattice.

Sulphur parallels with phosphorus in its ability to form a wide variety of allotropes in all the three phases. All the forms are not fully established. The interelationship among the various forms of sulphur was dealt in Class XI (Unit 13).

Liquid sulphur is an unusual liquid. It is pale golden and runny about 393 K, but it gets darker and thicker as it is heated. The sulphur molecules start to break up and form chains (S_n) which becomes tangled with one another with $n=6$, 7, 12, 18 and >20 in equilibrium (S_8 rings persists in liquid upto 465 K).

Sulphur vapour. The vapour contains S_n species with n from 2 to 10, with S_8 predominating at ~873 *k* while S_2 becomes dominant above 993 K. Like O_2, S_2 is paramagnetic.

Selenium exists in six allotropic modifications. Of these three are red monoclinic forms containing Se_8 rings. Unlike sulphur, it also exists as in a grey form which has the properties of a metalloid. This form is quite stable and consists of infinite spiral chains made of hexagonal monoclin·c form. Elemental selenium is used in photoelectric devices (xerography) in photoelectric cells and as a rectifier in semiconductor devices. The only form of tellurium known is silvery white, semi-metallic, and isomorphous with grey selenium.

10.8.1. Chemical Properties of Group 16 Elements and their Trends

As the second most electronegative element, oxygen reacts directly with all other elements except the noble gases, the halogens and the noble metals (Ag, Au, *etc.*) to form oxides.

$$2\,Mg\,(s) + O_2\,(g) \longrightarrow 2MgO\,(s)$$
$$P_4\,(s) + 5O_2\,(g) \longrightarrow P_4O_{10}\,(s)$$

All the group 16 elements act as oxidizing agents toward hydrogen. The oxidizing power decreases in the order : $O > S > Se > Te$.

Various non-metals that react with S, Se and Te include halogens, carbon, phosphorus, *etc.* The nature of the product with halogen depends upon conditions.

$$S + 3F_2 \rightarrow SF_6$$
$$S + 2X_2 \rightarrow SX_4$$

($X = F$, Cl, and Br; $SeBr_4$ and $TeBr_4$ with excess Br_2; Te only forms TeI_4).

Many compounds are oxidized to the oxides of their constituent elements.

$$2H_2S(g) + 3O_2(g) \longrightarrow 2H_2O(g) + 2SO_2(g)$$
$$2PbS(s) + 3O_2(g) \longrightarrow 2PbO(s) + 2SO_2(g)$$

As evident by electronegativity and ionization energy data, S, Se, and Te are less reactive than oxygen. They form chalcogenide ions by reaction with metals under drastic conditions.

10.8.2. Compounds of Group 16 Elements

Oxides. Group 16 elements form dioxides $M(IV)O_2$ and trioxides, $M(VI)O_3$. The dioxides are obtained by burning the elements in air. Sulphur dioxide is also produced when many sulphides are roasted in air. Usually SeO_2 and TeO_2 are prepared by heating the product obtained from the oxidation of Se or Te with concentrated HNO_3.

$$Se(s) + 4HNO_3 \longrightarrow SeO_2(s) + 4NO_2 + 2H_2O(l)$$

SO_2 is prepared in the laboratory by action of concentrated sulphuric acid on copper, or dilute acid on sulphites or bisulphites. Sulphur dioxide is a dense gas with a choking smell. It fumes in air and is extremely soluble in water. It dissolves in water to form a solution which contains sulphurous acid.

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$

The acid is weak and unstable. It decomposes to give SO_2. Sulphur dioxide combines with dioxygen in the presence of a platinized asbestos or vanadium pentoxide at a temperature of about 773K and at one atmospheric pressure.

$$2SO_2(g)+O_2(g) \xrightarrow[773K,\ atm]{V_2O_5} 2SO_3(g)$$

It behaves both as reducing and oxidizing agents. It (*i*) decolourizes $KMnO_4$, (*ii*) turns $Cr_2O_7^{2-}$ solution green, (*iii*) reduces Fe(III) to Fe(II), and (*iv*) reduces halogens to halides. Aqueous solution of SO_2 oxidizes H_2S.

$$2H_2S+\underset{(H_2O+SO_2)}{[SO_3^{2-}+2H^+]} \rightarrow 3H_2O+3S$$

It can bleach the colours of the substances because of its reducing nature.

Both SeO_2 and TeO_2 are soluble in water and form H_2SeO_3 and H_2TeO_3 respectively from which the oxides can be recovered by dehydration. Both SeO_2 and TeO_2 are white solids. They dissolve in aqueous solution of hydroxides to produce selenites and tellurites. They are better oxidizing agents and poorer reducing agents than the corresponding sulphur compounds. SeO_2 is employed in certain organic synthesis.

The dioxides are angular molecules with a delocalized π bond.

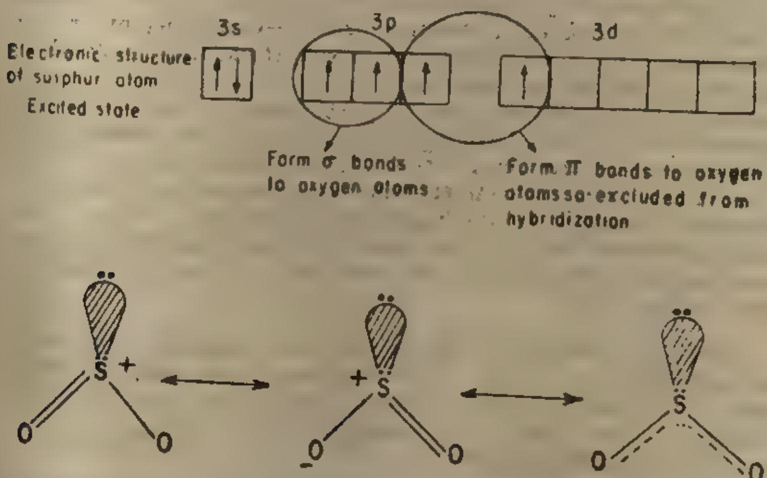
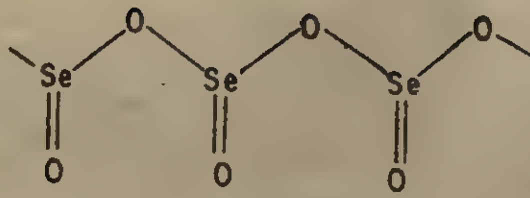


Fig. 10.26. Scheme of hybridization assumed by S in SO_2 and spatial arrangement of atoms in SO_2

SO_2 exists as discrete molecules in the gas, liquid and solid phases. The bond angle is 119.50°. This implies that the σ bonds involve orbitals of the sulphur atom which are close to sp^2 hybrid orbitals. Solid SeO_2 (volatile) forms infinite chains weakly bonded together.



SeO_2 chain lattice

In the vapour, discrete SeO_2 molecules exist which structurally resemble SO_2. Tellurium dioxide is a non-volatile solid and crystallizes in two forms, both apparently ionic lattices.

The dioxides can either donate or accept a pair of electrons and serve either as Lewis bases or Lewis acids.

Sulphur trioxide is obtained by the direct oxidation of SO_2 by oxygen usually in the presence of a platinum or vanadium pentoxide catalyst at 773K. It is an extremely reactive substance and a strong oxidizing agent. It is the anhydride of H_2SO_4 and reacts violently with water to produce the acid and with metallic oxides to produce sulphates. It dissolves in concentrated H_2SO_4 and forms pyrosulphuric acid, $H_2S_2O_7$ (fuming acid or oleum). At temperatures of 1173K or higher, SO_3 decomposes to SO_2 and O_2. Sulphur trioxide gas has a planar triangular structure with S—O distance of 141 pm. It involves sp^2 hydridization about sulphur atom. The molecule is symmetrical and has no dipole moment. It is considered to be a resonance hybrid involving $p\pi$—$p\pi$ S—O bonding (Fig. 10.27), with additional π bonding via overlap of filled oxygen $p\pi$ orbitals with empty sulphur $d\pi$ orbitals, to explain the S—O distance of 141 pm. In the solid state, the molecules polymerise and may form linear chains which have dispersion forces between adjacent layers. This form is asbestos—like in appearance. It is also possible to obtain a form containing cyclic molecules, consisting of three SO_3 linked as shown in Fig. 10.27.

SeO_3 is a white solid. It is extremely hygroscopic. It is an acid anhydride of H_2SeO_4. It is not very stable, sublimes readily above 373K and decomposes to SeO_2 and O_2 above 438K. It is prepared, in low yields, on passing electric discharge through selenium vapour and oxygen.

TeO_3 is prepared by heating telluric acid, H_6TeO_6 to a moderate temperature. It is an orange solid. It is insoluble in water, but dissolves in hot concentrated alkalis to form tellurates Selenium trioxide solid is a cyclic tetramer (Se_4O_{12}) as shown in Fig. 10.27. TeO_3 is a solid with a network structure in which TeO_6 octahedra share all vertices.

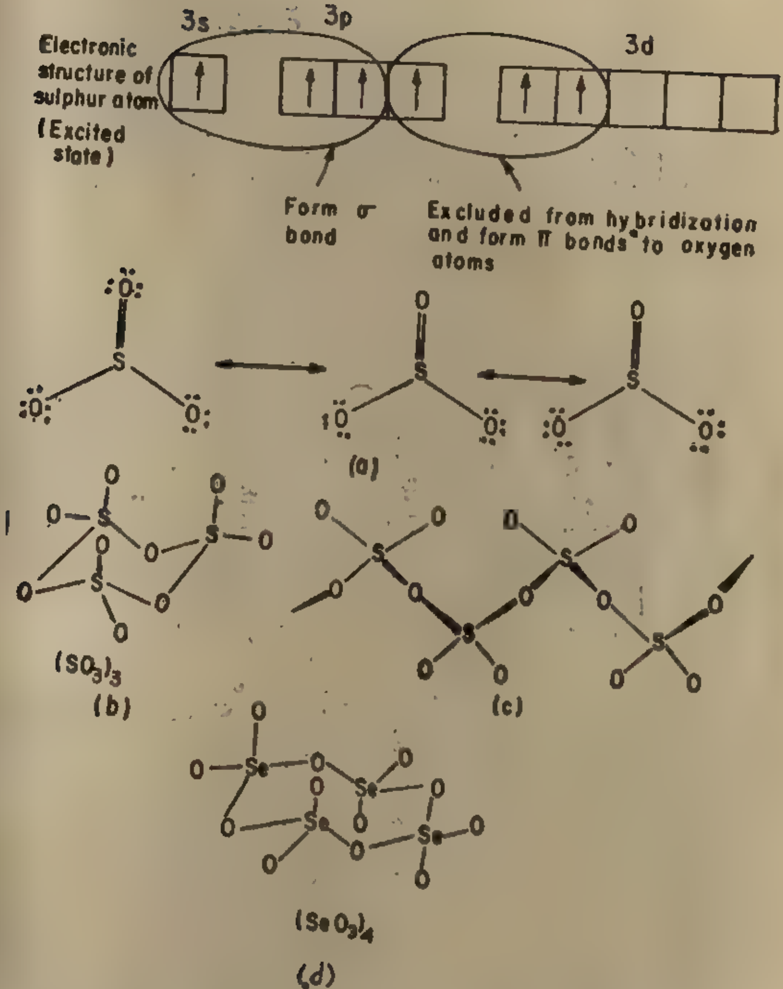
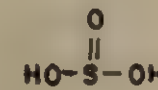
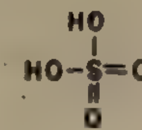
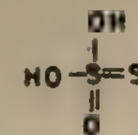
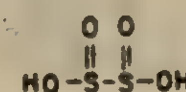
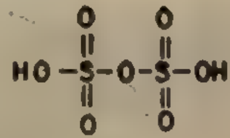
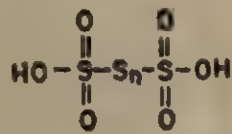
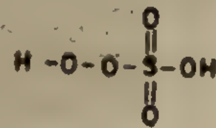
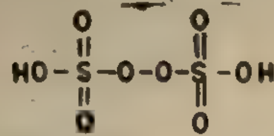


Fig. 10.27. Structures of (a) gaseous SO_2, (b) cyclic trimer of solid SO_3, (c) polymerized (linear chain) form of solid SO_3, and (d) cyclic tetrameric form of SeO_3

Oxoacids. A varied assortment of oxoacids of sulphur exists. The sulphur is mostly four coordinated and bonded to O=, HO—, —S— or sometimes —O—O—. Sulphur shows its tendency of catenation in its oxoacids. Some of the oxoacids are listed in Table 10.15.

Table 10.15 : Some oxyacids of sulphur

Number of sulphur atoms	*Acid (Oxidation of S)*	*Name*	*Preparation*	*Structure*
1	$H_2SO_3(+4)$	Sulphurous	SO_2+H_2O or acid on sulphites. Free acid does exist.	
	$H_2SO_4(+6)$	Sulphuric	SO_3+H_2O	
2	$H_2S_2O_3\begin{pmatrix}+6\\-2\end{pmatrix}$	Thiosulphuric	Sodium thiosulphate+HCl, Unstable at room temperature	
	$H_2S_2O_4(+4)$	Dithionous	Free acid unknown, with Zn reduction of H_2SO_3.	

Number of sulphur atoms	*Acid (oxidation state of sulphur)*	*Name*	*Preparation*	*Structure*
	$H_2S_2O_7(+6)$	Pyrosulphuric	$SO_3 + H_2SO_4$	
3 or more	$(H_2S_2O_6)S_n\begin{pmatrix}+6\\-2\end{pmatrix}$	Polythionic		
Peroxoacids	$H_2SO_5(+6)$	Peroxomonosulphuric	H_2O_2+chlorosulphuric acid (HO_3SCl).	
	$H_2S_2O_8(+6)$	Peroxodisulphuric	Anodic oxidation of HSO_4^-	

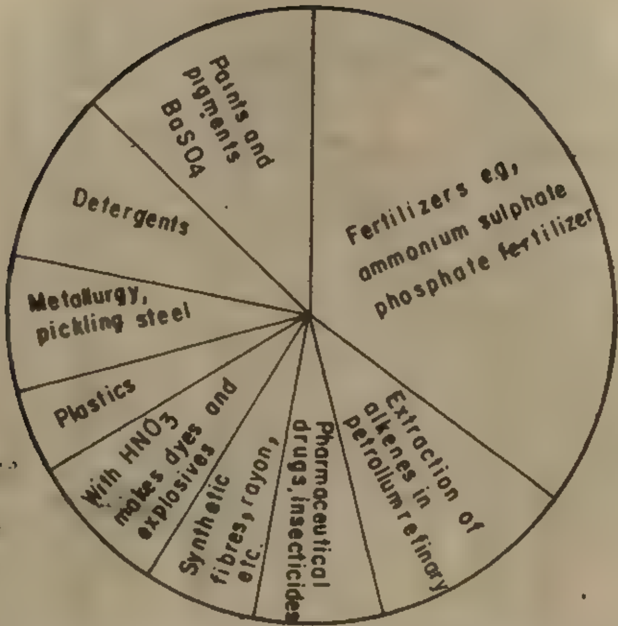


Fig. 10·28. Some industrial uses of sulphuric acid

Sulphuric acid is an extremely important industrial chemical (Fig. 10.28). Most of the acid is produced by the contact process, which involves the catalytic oxidation of SO_2 to SO_3.

$$2SO_2(g)+O_2(g) \xrightarrow[773K,\ 1\ atm]{Pt\ or\ V_2O_5} 2SO_3 \qquad (\Delta H=-98\ kJ)$$

When SO_3 is dissolved in water to form H_2SO_4, lot of heat is generated.

$$SO_3(g)+H_2O(l) \longrightarrow H_2SO_4(l) \qquad (\Delta H=-88\ kJ\ mol^{-1})$$

..e elevated temperature from the heat generated tend to produce mist, which prevents effective mixing of the two reactants. To avoid this problem, SO_3 is first dissolved in H_2SO_4 to give oleum or fuming sulphuric acid, $H_2S_2O_7$, which is then hydrolyzed to H_2SO_4 by adding water.

Pure anhydrous sulphuric acid is a colourless viscous oily liquid, also called 'oil of vitriol'. It has great affinity for water and even chars organic compounds containing hydrogen and oxygen as these are removed in proportion of water.

$$C_{12}H_{22}O+11H_2SO_4 \longrightarrow 12C+11\ (H_2SO_4.H_2O)$$

Sulphuric acid participates in two types of oxidation reactions : (*i*) those depending on the oxidizing powe- of the hydronium ion and

hence characteristic of acids in general, and (*ii*) those that involve sulphate portion of the acid, in which sulphur is reduced to +4 state.

$$Zn+[2H^{+}+SO_4^{2-}] \longrightarrow Zn^{2+}+SO_4^{2-}+H_2$$
$$C+2H_2SO_4 \longrightarrow CO_2+2SO_2+2H_2O$$

Sulphur dioxide is the usual product of reduction, but free sulphur and H_2S can also be produced. Copper metal reduces hot conc. H_2SO_4 to SO_2. It dissolves many compounds which can ionize as electrolytes in this medium. Its solvent potentialities are due to its high dielectric constant, polarity and ability to form hydrogen bonds. Anydrous H_2SO_4 undergoes autoprotolysis.

$$2H_2SO_4 \rightleftharpoons H_3SO_4^{+}+HSO_4^{-}$$

It also dissociates partially into H_2O and SO_3. Water, HNO_3, H_3PO_4, alcohols,. carboxylic acids, ketones, amines, *etc.* are protonated in H_2SO_4 and act as bases.

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^{+}+HSO_4^{-}$$
$$H_3PO_4+H_2SO_4 \rightleftharpoons P(OH)_4^{+}+HSO_4^{-}$$
$$(CH_3)_2\,CO+H_2SO_4 \rightleftharpoons (CH_3)_2\,COH+HSO_4^{-}$$
$$HNO_3+2H_2SO_4 \rightleftharpoons \underset{\text{Nitronium ion}}{NO_2^{+}}+H_3O^{+}+2HSO_4^{-}$$

The last reaction is helpful in nitrating organic compounds.

$$R-H+NO_2^{+}+2HSO_4^{-}+H_3O^{+}+ \longrightarrow RNO_2+2H_2SO_4+H_2O$$

Structure of Sulphuric Acid :

The structure of sulphuric acid in the vapour phase can be schematically portrayed as given in Fig. 10.29. Sulphate ion adopts tetrahedral disposition of oxygen atoms around sulphur atom. All the bond lengths are rather short (144 pm) because of resonance of the double bonds (Fig. 10.30) to give a resonance hybrid (Unit 13, class XI, textbook).

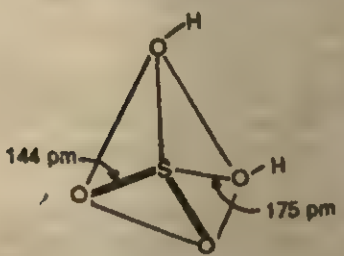


Fig. 10.29. Structure of $H_2SO_4(g)$

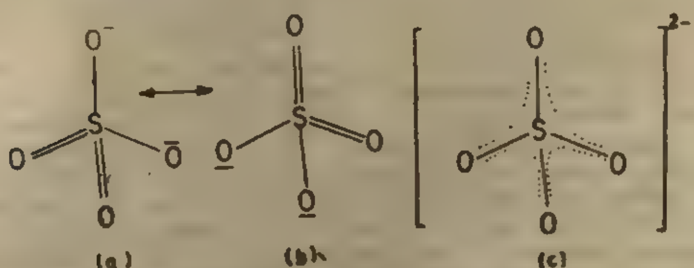


Fig. 10.30. Structure of SO_4^{2-} ion

In some cases the free acid has been made; in others, only the salts are known, *e.g.*, $H_2S_2O_3$ and $H_2S_2O_4$. The peroxo-acids and their salts contain the peroxo grouping —O—O— and are therefore very strong oxidizing agent.

Selenium and tellurium form oxyacids in which the elements are in the +4 and +6 states. SeO_2 reacts with water to give selenous acid, H_2SeO_3. Free tellurous acid, H_2TeO_3 does not appear to exist. Selenous acid can be converted into selenic acid, H_2SeO_4 by powerful oxidizing agents.

Sulphuric and selenic acids are strong, but telluric acid is a weak dibasic acid. Structurally, telluric acid differs from the others having six OH groups arranged octahedrally about the Te atom; *i.e.* $Te(OH)_6$.

Hydrides. All elements of this group form simple volatile binary hydrides of the H_2X(X=O, S, *etc.*) type. The simple hydride of oxygen is H_2O. Another known hydride of oxygen is H_2O_2. Sulphur forms the most extensive series of catenated hydrides such as H_2S_2, H_2S_2, H_2S_4, *etc.*, Hydrides of sulphur, other than H_2S, are all yellow oils which readily decompose into H_2S and free sulphur.

Water (H_2O), the simple hydride of oxygen is a unique compound. It is the most abundant liquid. It has an extraordinarily high melting and boiling points compared to the other hydrides of the group. As ice, it is less dense than liquid water. Its density varies with temperature and is maximum at 277K.

Its uniqueness is attributed to high polarity and hydrogen bonding (due to highly electronegative oxygen atom). Water is an acid, a base, a coordinating molecule, an oxidizing agent and a reducing agent (rarely).

Hydrogen sulphide (H_2S) is usually prepared by taking together iron (II) sulphide and dilute H_2SO_4. Hydrogen selenide (H_2Se) and hydrogen telluride (H_2Te) can be prepared by the action of dilute acids on certain metallic selenides and tellurides respectively.

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

All hydrides except water are offensive smelling colourless gases at ordinary temperature. They are extremely toxic. Aqueous solutions of these hydrides are feebly acidic. They are stronger acid than water (acid strength : $H_2Te > H_2Se > H_2S$). The acid strength increases with decreasing bond strength of the hydride. The boiling and melting points of H_2S, H_2Se and H_2Te are much lower than water (Fig. 10.31) indicating that the effect of molecular association through hydrogen bonding (Fig. 10.32) is maximum in the case of water. The bond angles in these hydrides are all close to 90° (except H_2O).

Their reducing power increases whereas their thermal stability decreases in the order : $H_2O < H_2S < H_2Se < H_2Te < H_2Po$. In fact H_2Te and H_2Se are better reducing agents than hydrogen. Some of the physical properties of the hydrides are summarized in Table 10.16 and Fig. 10.31.

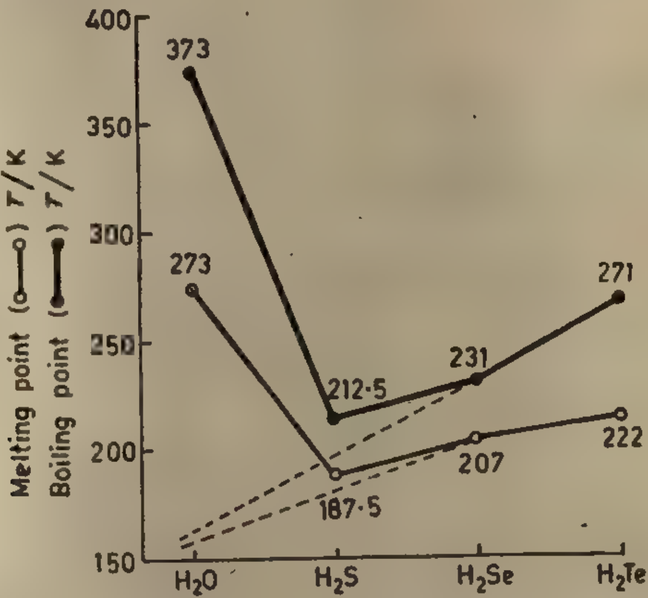


Fig. 10.31. Melting and boiling points of the hydrides of the group 18 elements.

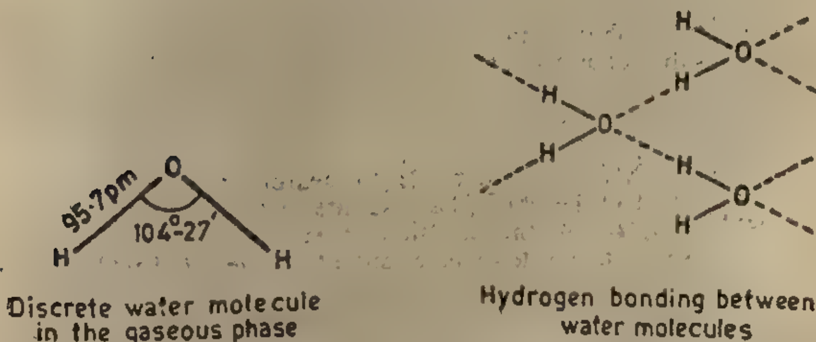


Fig. 10.32. Water molecule and Hydrogen bonding between water molecules.

TABLE 10.16 : Some physical properties of binary hydrides

Hydride	*Physical state at 298 K*	*Heat of formation* ΔH_f/kJ mol^{-1}	*Heat of vaporization* ΔHv/kJ mol^{-1}	*Bond dissociation energy for M-H,* *BE*/kJ mol^{-1}	*Bond angle HMH*
H_2O	Liquid	−242	40.8	466.2°	104°
H_2S	Gas	−20.2	18.7	340.6°	92°
H_2Se	Gas	+85.8	19.9	277.6°	91°
H_2Te	Gas	+154.4	24.0	241.5°	90°

Halides. The elements of group 16 form a variety of halides. Many of them are listed in Table 10.17.

Only fluorides of oxygen are known. Other halogens (Cl_2, Br_2 and I_2) are more electropositive than oxygen; the binary compounds are better regarded as oxides of halogens and are accordingly named.

TABLE 10.17 : Binary halides of group 16 elements

Element	*Fluorides*	*Chorides*	*Bromides*	*Iodides*
O	F_2O_2,F_2O	Cl_2O, ClO_2, Cl_2O_6, Cl_2O_7	Br_2O, BrO_2, BrO_3	I_2O_4 I_4O_9, I_2O_5
S	S_2F_2,SF_4, SF_6, S_2F_{10}	S_2Cl_2,SCl_2, SCl_4	S_2Br_2	—
Se	Se_2F_2,SeF_4, SeF_6	Se_2Cl_2,$SeCl_4$	Se_2Br_2, $SeBr_4$	—
Te	TeF_4, TeF_6	$TeCl_2$, $TeCl_4$	$TeBr_2$, $TeBr_4$	TeI_4
Po	—	$PoCl_2$,$PoCl_4$	Po_2Br_2,$PoBr_4$	PoI_4

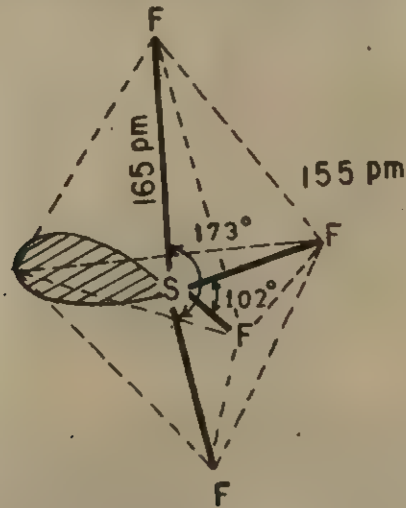
Oxides of halogens, including fluorides of oxygen, are all covalent. They are unstable except OF_2 and I_2O_5. All, except fluorides of oxygen, are formally acid anhydrides or mixed acid anhydrides. Many of the halogen oxides reat with water to give the corresponding oxyacid or mixture of oxyacids. They also react with basic solution to give the salt or mixture of salts of the corresponding oxyacids.

Sulphur forms halides of the type MX_2, MX_4 and MX_6. Halides of sulphur with S—S bond are also formed. All the halides, with the exception of SF_6 (inert ; d^2sp^3 hybridization), are hydrolyzed by water with a varying degree of success. They are covalent compounds with low boiling points. They are chemically active compounds.

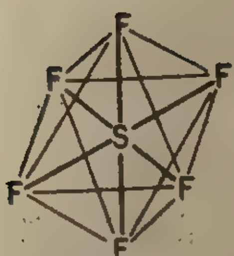
SeF_6 and TeF_6 are susceptible to hydrolysis. Tetrafluorides are less stable than hexafluorides and are hydrolyzed by water to give HF and MO_2. As the electronegativity of the central atom decreases, the hexafluoride becomes more reactive. Other halides, similar to sulphur, are known for Se and Te. These compounds are generally more stable than the corresponding sulphur compounds.

Sulphur hexafluoride is extremely inert. It assumes octahedral structure (Fig. 10.33) with S-F bond distance of 155 pm. It is

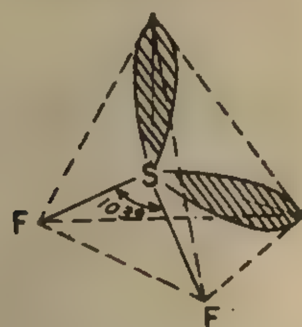
obtained by combustion of sulphur in a stream of fluorine. Because of its chemical inertness and dielectric strength, it is used as a gaseous insulator in high-voltage generators and switch gears. Sulphur tetrafluoride is a highly reactive gas. It is prepared by the action of NaF on sulphur dichloride in acetonitrile. It is used as a fluorinating agent for several inorganic and organic compounds. Its structure is based upon trigonal bipyramidal distribution of five electron pairs (four bonding pairs and one lone pair). The final shape assumed by the molecule is see-saw (Fig 10.33).



See Saw shape of SF_4



Octahedral shape of SF_6



Angular shape of SF_2

Fig. 10.33. Shapes of some halides of sulphur.

Sodium thiosulphate. It is the sodium salt of thiosulphuric acid which may be regarded as sulphuric acid in which one oxygen is replaced by a sulphur atom. The two sulphur atoms of thiosulphate ion are not equivalent ; one is in oxidation state +6 whereas other is in state —2.

Sodium thiosulphate, also called hypo, is obtained due to catenation property of sulphur, when sulphur is added to sodium sulphite, $Na_2SO_3+S \longrightarrow Na_2S_2O_3$.

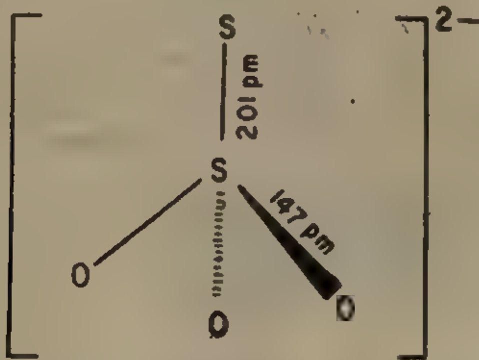


Fig. 10.34. Thiosulphate ion $S_2O_3^{2-}$

Many cations form complex ions with thiosulphate ions, the silver ion, Ag^+, for example, forms the soluble anion $[Ag(S_2O_3)_2]^{3-}$ and silver salts are therefore soluble in this thiosulphate solutions.

$$AgBr(s)+2S_2O_3^{2-}(aq) \longrightarrow [Ag(S_2O_3)]^{3-}(aq)+Br^-(aq)$$

This reaction is used in photography to remove unreacted light sensitive silver bromide from photographic plates to avoid further reaction with light. Thousulphates disproportionate on heating, *e.g.*,

$$4Na_2S_2O_3(s) \longrightarrow 3Na_2SO_4(s)+Na_2S(s)+4S$$

Thiosulphates are mild reducing agents, for example, they reduce I_2 to I^-, $Fe^{3+}(aq)$ to $Fe^{2+}(aq)$, *etc*. The reaction with I_2 to yield tetrathionate, $S_4O_6^{2-}$ is rapid and quantative and is useful in volumetric estimation of I_2.

$$I_2+2S_2O_3^{2-} \longrightarrow S_4O_6^{2-}+2I^-$$

10.9. GROUP 17 ELEMENTS : THE HALOGEN FAMILY

Flourine (F), Chlorine (Cl), bromine (Br) and iodine (I) are collectively known as halogens. The name halogen is derived from Greek word 'halos' which means 'sea salt former'. This reflects that most of these elements exist in sea water in the form of salts. These elements constitute group 17 of the periodic table. Astatine, the last element in this group is radioactive. Its properties seem to

follow the trend in the halogen family. Little is known about astatine due to its radioactive nature and short half-life ; the longest lived nuclide is 210 with a half-life of 8 hr.

All halogens exist as diatomic molecules at ordinary conditions. The molecules are held together by van der Waals forces (weak forces). The strength of these forces increases with increasing size of molecules. Thus, the physical state these elements changes from gas to liquid to solid (Table 10.18). Because of the increasing van der Waals forces, the melting and boiling points of the halogens inerease from fluorine to iodine.

They are all coloured because they absorb light in the visible region resulting in the excitation of outer electrons to higher energy levels. The sm ller the atom, more will be the energy needed for excitation. Gaseous F_2 molecules absorb high energy violet light and appear violet. Similarly, chlorine molecules appear yellow-green and bromine molecules reddish-brown (Table 10.18).

The members of the family are very similar in chemical behaviour, since they all have seven electrons in the valence shall, ns^2 np^5. They have only one electron less than the number present in the adjacent noble gas. They can acquire a noble gas electronic configuration by :

(*i*) accepting one electron from a donor group, and

$X+e^- \longrightarrow X^-$, as in Na^+Cl^-, K^+I^-, *etc.*

(halogen atoms become stable univalent ions)

(*ii*) forming a single covalent bond as in the halogen molecules (X—X) and hydrogen halides (H—X).

Each halogen is the most reactive non-metal of its period as depicted by electrode potential data. Their non-metallic nature slowly decreases down the group and iodine acquires some metallic character. It has a metallic lusture.

All the halogens show -1 oxidation state. Fluorine is the most electronegative of all the halogens. It shows only -1 oxidation state. Other halogens exhibit $+1$, $+3$, $+5$ and $+7$ oxidation states. In interhalogen compounds (ClF, BrF, ICl, *etc.*) halogens (except F) show $+1$ oxidation state. The higher oxidation states shown by Cl, Br and I is attributed to the presence of vacant d orbitals in their valence shell. The negative oxidation state of -1 decreases in stability relative to the element as we move from Cl$\longrightarrow$Br$\longrightarrow$I and the positive oxidation states progressively become more stable (due to decreasing ionization energy). The halogens show a general gradation in their properties, the first two members are gaseous, bromine is a liquid and iodine is a solid at ordinary temperatures. The ionization energies, electron affinities and electronegativities decrease gradually from fluorine to iodine.

The electron affinity of chlorine is maximum. The ow value of fluorine appears to be due to electron-electron repulsion of the small and highly dense electron cloud of the fluorine atom.

TABLE 10.18 : Atomic and molecular properties of halogens

Property	*F*	*Cl*	*Br*	*I*
Atomic number	9	17	35	53
Electron structure	$[He]2s^2 2p^5$	$[Ne]3s^2 3p^5$	$[Ar]3d^{10} 4s^2 4p^5$	$[Kr]4d^{10} 5s^2 5p^5$
Covalent radius r/pm	72	99	114	103
Ionic radius, X^- r^-/pm	136	181	195	216
Electron affinity/ kJ mol^{-1}	333	349	325	296
Ionization energy, *IE*/kJ mol^{-1}	1681	1255	1142	1007
Electronegativity	4.0	3.0	2.8	2.5
Oxidation states	−1	−1, +1, −3, +3, +4, +5, +7	−1, +1, +3, +5, +7, +4	−1, +1, −3, +5, +7, +4
	F_2	Cl_2	Br_2	I_2
Melting point, *T*/K	53	172	266	306
Boiling point, *T*/K	85	238	332	456
Density, liquid state ρ/g cm^{-3}	1.51 85K	1.66 203K	3.2 273K	3.96 493K
Physical state	Gas	Gas	Liquid	Solid
Colour	Pale yellow	Greenish yellow	Reddish brown	Greyish black
Bond distance X—X *l*/pm	143	199	228	266
Bond dissociation energy, *E*/kJ mol^{-1}	159	243	193	151
Heat of vaporization, ΔHvap/kJ mol^{-1}	6.54	20.41	29.56	41.95
Electrode potential at 298K, $E°$/V $X_2 + 2e^- \longrightarrow 2X^-(aq)$	+285	+1.36	+1.07	+0.55

10.9.1. Chemical Properties of Halogens and their Trends

The halogens undergo a variety of chemical reactions. Some typical reactions of the halogens are given below :

Halogens are excellent oxidizing agents. Flourine is the most electronegative element, *i.e.*, the strongest electron acceptor, and therefore, is the strongest oxidizing agent. The oxidizing action of the halogens decrease in the order of F>Cl>Br>I. This relative oxidizing power is well evident in the displacement reactions. The order of oxidizing power not due to the electron affinities (the value

of electron affinity is the highest for Cl), but is mainly due to the relative hydration energies ΔH_{hyd}/k J mol^{-1} F(−460), Cl(−385), Br(−351), I(−305) and to a lesser extent to the weak dissociation energy of F—F bond (Table 10.18).

$H_2S+X_2(aq) \longrightarrow 2HX+S$	X=Cl, Br, I
$8NH_3+3X_2 \longrightarrow 6NH_4X+N_2$	X=Cl, Br
$2H_2O+2F_2 \longrightarrow 4HF+O_2$	Vigorous reaction
$H_2O+Cl_2 \longrightarrow HCl+HClO$	Rapid reaction
$H_2O+Br_2 \longrightarrow HBr+HBrO$	Slow reaction. No reactton with I_2
$F_2+2NaX \longrightarrow 2NaF+X_2$	X=Cl, Br, I; F_2 displaces all other halogens from their halides.
$Cl_2+2NaX \longrightarrow 2NaCl+X_2$	X=Br, I; Cl_2 displaces Br_2 and I_2.
$Br_2+2NaI \longrightarrow 2NaBr+I_2$	Br_2 displaces I_2. I_2 does not displace any other halogen.

All halogens react with water at different rates. F_2 reacts vigorously and instantaneously with water to give HF and some other products, *e.g.*, OF_2.

Chlorine, bromine and iodine react with water to yield hydrohalic acid (HX) and hypohalous acid (HOX).

$$X_2+H_2O \longrightarrow HX+HOX$$

HOCl is formed and only slowly decomposes to give HCl and oxygen. Decomposition becomes fast in the presence of sunlight.

$$2HOCl \xrightarrow{\text{Light}} O_2+2HCl$$

HOBr behaves in a similar way.

Halogens react with hydrogen at varying speed. Reactions with fluorine and chlorine are explosive. Chlorine combines with hydrogen slowly in the dark. The reaction between Br_2 and H_2 take place only in the presence of Pt at 473K. With iodine the reaction is incomplete even in the presence of Pt catalyst.

10.9.2. Compounds of Group 17 Elements

Oxides. The halogen oxides are all highly reactive, if not actually unstable, compounds. Halogens do not combine directly with oxygen. However, binary oxides can be prepared by indirect methods. They are endothermic compounds.

A large number of oxides of halogens have been characterized. Various binary oxides together with the formal oxidation number of the halogens are listed in Table 10·19.

Since fluorine is more electronegative than oxygen, the oxides are appropriately regarded as oxygen fluorides. The best known of the three oxides is oxygen difluoride, OF_2. The preparation and properties of some important oxides are summarized in Table 10.20.

TABLE 10.19 : Oxides of the halogens

Name	*F*	*Cl*	*Br*		*Oxidation state*
Monoxide	OF_2	Cl_2G(g)	Br_2O(g)	...	+1
	O_2F_2	...	...	...	+2
Trioxide	O_2F_2	Cl_2O_3(s)	...	...	+3
Dioxide		ClO_2(g)	BrO_2	I_2O_4	+4
Pentoxide		...	...	I_2O_5(s)	+5
Hexoxide		Cl_2O_6(l)	BrO_3(?)	...	+6
Heptoxide		Cl_2O_7(1)	Br_2O_7(?)	I_2O_7(s)	+7

TABLE 10.20 : *Group VII Oxides*

Oxide	*Preparation*	*Comments*
OF_2	$F_2+NaOH \longrightarrow OF_2$ (2% NaOH) solution	Explosive ; powerful oxidizing agent. Reacts with water to form O_2 and HF.
O_2F_2	$O_2+F_2 \xrightarrow[\text{Electric discharge}]{\text{High voltage}} O_2F_2$	Decomposes above 223K. Powerful oxidizing and fluorinating-agent.
Cl_2O	$2Cl_2+2HgO \rightarrow HgCl_2.HgO+Cl_2O$	Yellow gas, explosive and power ful oxidizing agent. Acidic in water gives $HClO$.
ClO_2	$2NaClO_3+H_2SO_4 \rightarrow 2ClO_2+2NaHSO_4$, or various commercial processes.	Explosive ; powerful oxidizing agent ; odd electron compound. Weakly acidic. Used as bleaching agent, e g., for wood pulp.
Cl_2O_6	$2ClO_2+O_3 \rightarrow Cl_2O_6+\frac{1}{2}O_2$	Decomposes at its melting point Acidic.
Cl_2O_7	$2HClO_4+P_4O_{10} \rightarrow Cl_2O_7$	Most stable of chlorine oxides. Acidic : in water gives back $HClO_4$.
Br_2O	$2HgO+2Br_2$ in $CCl_4 \rightarrow Br_2O+HgBr_2.HgO$	Above 233K gives Br_2+O_2 ; good oxidizing agent.
BrO_2	$Br_2+2LiO_3 \xrightarrow[195\text{ K}]{\text{Fluorocarbon}} 2BrO_2+Li_2O_2$	Also unstable above 233 K.
I_2O_5	$2HIO_3 \xrightarrow{473\text{ K}} I_2O_5+H_2O$	Acidic ; strong oxidizing agent, reacts with CO to give I_2+CO_2. used to estimate CO by titrating the iodine liberated.

Most of the oxides except OF_2 and I_2O_5 are unstable. All the lower oxides are highly explosive compounds. Stability increases with molecular complexity and oxidation states. The iodine oxides are the most stable. They are all covalent due to small difference in electronegativity between the halogens and oxygen.

All, except OF_2, are formally acid anhydrides or mixed acid anhydrides. They react with water to give corresponding oxyacid or mixture of oxyacids, *e.g.*,

$$Cl_2O(g) + H_2O(l) \longrightarrow HOCl(aq)$$
$$Cl_2O_6(s) + H_2O(l) \longrightarrow HClO_3(aq) + HClO_4(aq)$$
$$Cl_2O_7(s) + H_2O(l) \longrightarrow HClO_4(aq)$$
$$2ClO_2(g) + H_2O(l) \longrightarrow HClO_2(aq) + HClO_3(aq)$$

The most important compound of this group is ClO_2, a powerful oxidant, is used commercially as a bleach and in water purification. It is generated when needed by the reduction of chlorate satls.

$$2ClO_3^-(aq) + SO_2(g) + H^+(aq) \longrightarrow 2ClO_2(g) + HSO_4^-(aq)$$

In most of the oxides, oxygen is in the +2 oxidation state, and thus the oxides are potent oxidizing agent. They react with alkali to give a salt or a mixture of salts of the corresponding oxyacids, *e.g.*,

$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$
$$I_2O_5 + 2NaOH \longrightarrow 2NaIO_3 + H_2O$$

The oxides of iodine are solid involatile substances which are not comparable with the oxides of the ligher halogens in their chemical properties. I_2O_5 is the only true oxide. Iodine oxides I_2O_4 and I_4O_9 are ionic and salt-like in nature. They can be regarded as iodate compounds of iodine.

$$I_2O_4 : \quad IO^+IO_3^-$$
$$I_4O_9 : \quad I^{3+}(IO_3^-)_3$$

The structures of some of the representative oxides are given with sp^3 disposition around either O or X (Fig. 10.35).

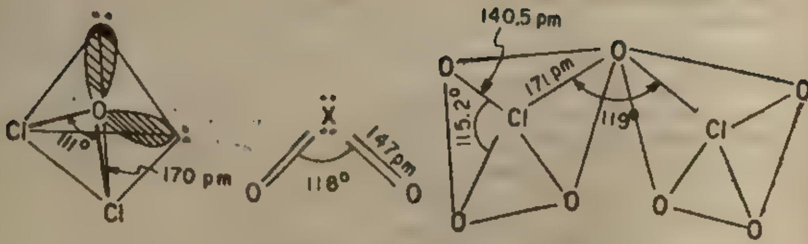
Oxoacids. Each of the halogens, except fluorine, forms four series of acids (HIO_2 is not known) having formulae :

$$HXO,\ HXO_2,\ HXO_3 \text{ and } HXO_4.$$

These are listed in Table 10.21 with the formal oxidation number.

TABLE 10.21 : Oxyacids of the halogens

Name	*F*	*Cl*	*Br*	*I*	*Oxidation state*
Hypohalous acid	HOF	HOCl	HOBr	HOI	+1
Halous acid		$HClO_2$	$HBrO_2$ (?)	—	+3
Halic acid		$HClO_3$	$HBrO_3$	HIO_3	+5
Perhalic acid		$HClO_4$	$HBrO_4$	HIO_4	+7



Cl_2O ClO_2 Cl_2O_7

Angular shape

Angular shape (Paramagnetic with odd number of electrons)

Fig. 10.35. Structure of the representatives of oxides of halogens.

The HOF molecule differs from the others in that the fluorine is not in a positive oxidation state but rather in a−1 state. As expected HOF is very unstable, and with oxygen in a zero oxidation state is a potent oxidizing agent. It is formed by passing fluorine over ice.

$$F_2(g) + H_2O(s) \longrightarrow HOF(g) + HF(g)$$

HOF is rapidly oxidized in water, but for the others the aqueous solutions are stable. The acids, like the oxides have oxidizing properties.

The **hypohalous acids** are weak acids. They are formed by the disproportionation of the hologens in water :

$$X_2 + H_2O \rightleftharpoons HOX + HX$$

Their aqueous solutions can also be made by passing the halogen into a well stirred suspension of mercuric oxide.

$$2X_2 + 2HgO + 2H_2O \longrightarrow HgO.HgX_2 + 2HOX$$

The three (except HOF) hypohalous acids may be obtained as salts by the direct action of halogen on cold aqueous alkali. The acids are less stable than their salts and the stability and the acid strength both decrease as the size of the halogen increases and the electronegativity of the halogen atom decreases :

$$HOCl > HOBr > HOI$$

Salts of hapohalous acids are known as hypohalites. Hypochlorites are made on a large scale for use as bleaching and sterilizing agents. The reaction of slaked lime with chlorine gives bleaching powder which has the composition,

$$Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$$

In aqueous solution, OX^- ions decompose as follows :

$$3XO^- \longrightarrow 2X^- + XO_3^-$$

Disproportionation of OCl^- and OBr^- ions in basic solution at 300K leads to the formation of halates :

$$3\,XO^- \longrightarrow XO_3^- + 2X^-$$

For OI^- ions, decomposition in solution is very fast even at room temperature. At this temperature the reaction of Cl_2 or Br_2 with solutions of alkali will also produce XO_3^- and X^-.

$$3X_2 + 6OH^- \longrightarrow XO_3^- + 5X^- + 3H_2O$$

Of the halous acids, only $HClO_2$ exists with certainty. The acid as well its satls are not very stable. The free acid even in solution decomposes readily.

$$8HClO_2 \longrightarrow 6ClO_2 + Cl_2 + 4H_2O$$

The salts, chlorites, are good oxidizing agents. Sodium chlorite is used as a bleaching agent. It is obtained when chlorine dioxide reacts with sodium peroxide.

$$2ClO_2 + Na_2O_2 \longrightarrow 2NaClO_2 + O_2$$

Among the **halic acids**, iodic acid is more stable than both chloric and bromic acids. It is obtained as a white crystalline solid by the oxidation of iodine with chloric acid solution.

$$HClO_3(aq) + I_2 \longrightarrow HIO_3\,(s) + ICl$$

$$HClO_3\,(aq) + ICl \longrightarrow HIO_3\,(s) + Cl_2$$

Solution of chloric acid, $HClO_3$ can be prepared by adding H_2SO_4 to a solution of barium chlorate.

$$Ba(ClO_3)_2\,(aq) + H_2SO_4 \longrightarrow BaSO_4\,(s) + 2HClO_3\,(aq)$$

Chlorates are commercially prepared by the electrolysis of hot concentrated solution of a chloride.

Free $HClO_3$ acid $HBrO_3$ exist only in solution and concentration causes decomposition. As stated above under hypohalous acids, halates can be obtained by reacting free halogen with hot alkali. Halic acids are strong acids but are weaker oxidizing agents than hypohalous acids. Chlorates disproportionates on heating (in the absence of a catalyst).

$$4KClO_3\,(s) \xrightarrow{\text{Heat}} 3KClO_4\,(s) + KCl\,(s)$$

The decomposition of $KClO_3$ is catalysed by MnO_2 evolving oxygen.

$$2KClO_3(s) \xrightarrow[MnO_2]{\text{Heat}} 2KCl\,(s) + 3O_2\,(g)$$

When SO_2 is passed through an aqueous solution of a chlorate, ClO_2 is produced. Halates react with halides in acid medium to give halogens.

$$XO_3^- + 5X^- + 6H^+ \longrightarrow 3X_2 + 3H_2O$$

Sodium and potassium chlorates are made on an industrial scale. Both sodium and potassium chlorates are used in fireworks and safety matches.

Potassium iodate, KIO_3 is used as primary standard in iodometric titrations. In acid solution, it reacts with potassium iodide and liberates iodine quantitatively :

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

Perhalates are prepared by the oxidation of halate salts,

$$ClO_3^-\ (aq) + H_2O\ (l) \xrightarrow{\text{Electrolysis}} ClO_4^-\ (aq) + 2H^+\ (aq) + 2e^-$$

$$BrO_3^-\ (aq) + F_2(g) + 2OH^-\ (aq) \longrightarrow BrO_4^-\ (aq) + 2F^-(aq) + H_2O(l)$$

$$IO_3^-\ (aq) + Cl_2\ (g) + 2OH^-\ (aq) \longrightarrow IO_4^-(aq) + 2Cl^-\ (aq) + H_2O(l)$$

The acids are produced from the perhalate salts. They are powerful oxidizing agents and reactionss may be explosive. Perchloric acid is one of the strongest acids known. The perhalates are strong oxidizing agents, the oxidizing ability varying in the order $ClO_4^- < BrO_4^- > IO_4^-$. Perchloric and periodic acids are among the strongest acids.

Oxyacids become more stable and stronger as the number of unprotonated oxygen atoms per molecule increases. As a result, oxidation state of the halogen increases. The strength of the acid increases with increase in positive oxidation state.

Thus, the strength and stabilily of the four oxyacids of chlorine follow the sequence.

$$HClO < HClO_2 < HClO_3 < HClO_4$$

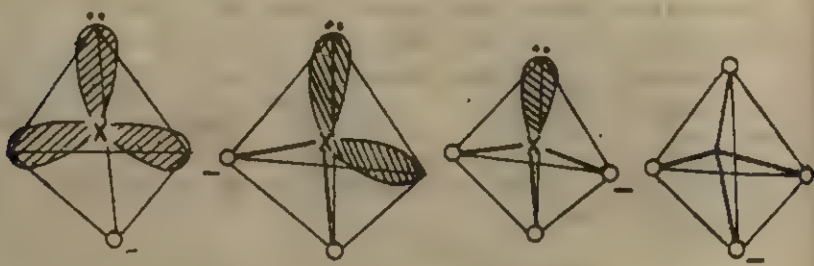


Fig. 10.36. Structures of various oxyanions present in oxyacids

Halides. Most of the elements (except, He, Ne and Ar) form binary halides which differ in their stoichiometries and structural

types. The compounds cover the whole range from ionic or semi-ionic polymeric lattices to discrete molecules that form van der Waals crystals. Figure 10 37 suggests the broad divisions between the various types of halides. The ionic character of a metal halide decreases from the flouride to the iodide :

$$M{-}F > M{-}Cl > M{-}Br > M{-}I$$

It has been seen that, if a metal exhibits more than one oxidation state, the halide in the higher oxidation state is more covalent than the one in the lower oxidation state. Accordingly $SnCl_4$, $PbCl_4$, $SbCl_5$, UF_6 have been found to be more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$

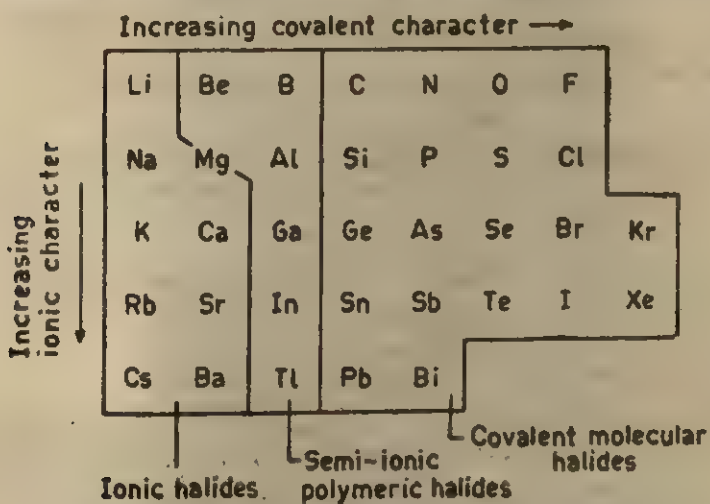


Fig. 10.37. Classification of halides on the basis of bonding and structural properties of the halides of the elements.

and UF_4, respectively. It has also been seen that F^- stabilises highest oxidation states of metals (*e.g.*, WF_6, OsF_8), while I^- stabilises lower oxidation states.

$$2Fe + 3F_2 \longrightarrow 2Fe(III)\,F_3$$

$$\underset{\text{(Excess)}}{2Fe + 3Cl_2} \longrightarrow 2Fe\,(III)\,Cl_3$$

$$\underset{\text{(Limited)}}{Fe + Cl_2} \longrightarrow Fe\,(II)\,Cl_2$$

$$Fe + I_2 \longrightarrow Fe\,(II)\,I_2\ \text{(only)}$$

$$Fe^{3+} + I^- \longrightarrow Fe^{2+} + \tfrac{1}{2}I_2$$

$$Cu + X_2 \longrightarrow Cu\,(II)\,X_2\ (X = Cl,\ Br,\ I)$$

$$2Cu + I_2 \longleftrightarrow 2Cu\,(I)\,I$$

$$Cu^{2+} + 2I^- \longrightarrow Cu\,(I)\,I + \tfrac{1}{2}\,I_2$$

Trends in the bonding and structures of halides are indicated by the trends in their boiling and melting points Fig. (10.38), which suggest about the strength of intermolecular forces. The boiling points of the molecular compounds increase from fluorides to iodides because of mass increase. In the case of ionic halides the reverse trend is observed because of the influence of lattice energy. An important group of these compounds comprises the hydrogen halides which exist as covalent diatomic molecules in the gas phase ; they dissolve in water to form hydrohalic acids.

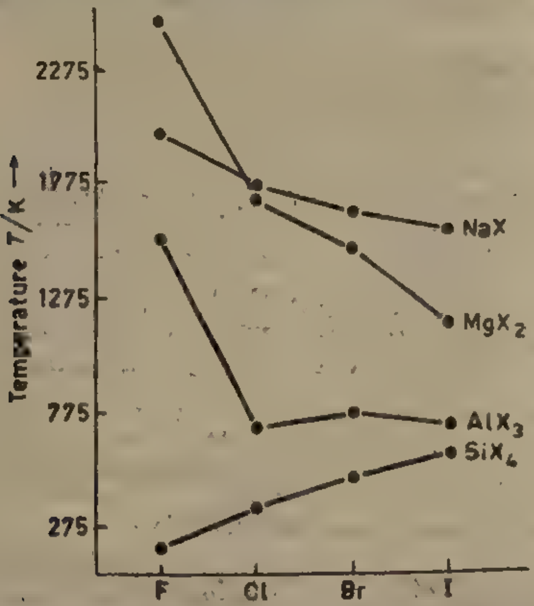


Fig. 10.38. Boiling points of some representative halides.

Hydrogen Halides (Hydrides). Binary hydrides of halogens can be prepared by the direct union of their constituent elements under appropriate conditions.

Commercially hydrogen fluoride and hydroge chloride are produced by heating fluorid uorspar) and chlorides with concentrated sulphuric acid.

$$CaF_2(s)+H_2SO_4(aq) \xrightarrow{\text{Hot}} CaSO_4(s)+2HF(g)$$
$$NaCl(s)+H_2SO_4(aq) \longrightarrow NaHSO_4(s)+HCl(g)$$
$$NaHSO_4(s)+NaCl(aq) \longrightarrow Na_2SO_4(aq)+HCl(g)$$

These methods are also employed for the laboratory preparation of HF and HCl. In the preparation of HBr and HI, this method gives

rise to certain undesirable products, hence, is not used. Both HBr and HI reduce H_2SO_4.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$
$$H_2SO_4 + 2HBr \longrightarrow 2H_2O + SO_2 + Br_2$$
$$H_2SO_4 + 2HI \longrightarrow 2H_2O + SO_2 + I_2$$

Hydrogen halides can also be prepared by the hydrolysis of covalent halides of certain non-metals. PCl_3, PBr_3, PI_3 and SCl_4 generally react with water to form two acids—the HX and an oxyacid of the non-metal other than halogen. HBr and HI are generally prepared on these lines.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$
$$SCl_4 + 3H_2O \longrightarrow H_2SO_3 + 4HCl$$

Pure HF can be prepared by heating potassium hydrogen fluoride.

$$KHF_2 \longrightarrow KF + HF$$

Aqueous HBr and HI can be prepared by the reduction of the elemental halogen by means of H_2SO_3 or H_2S.

$$Br_2 + H_2S \longrightarrow 2HBr + S$$
$$Br_2 + H_2SO_3 + H_2O \longrightarrow 2HBr + H_2SO_4$$
$$I_2 + H_2S \longrightarrow 2HI + S$$
$$I_2 + H_2SO_3 + H_2O \longrightarrow 2HI + H_2SO_4$$

At room temperature all the hydrogen halides are colourless gases with anirritating odour. Like the elements, the binary hydrides show similarities and regular trends in properties (Table 10.22). They

TABLE 10.22 : Some physical properties of binary hydrides

Property	*HF*	*HCl*	*HBr*	*HI*
Physical state at 288 K	Liquid	Gas	Gas	Gas
Melting point, T/K	190	158.4	186	222
Boiling point, T/K	292.5	189	206	238
Heat of formation, ΔH_f/kJ mol^{-1}	−270.9	−92.4	−30.67	−5.55
Bond energy, BE/kJ mol^{-1} $HX(g) \longrightarrow H(g) + X(g)$	566	431	366	299
Bond length/l pm	86	128	142	160
Heat of vaporization, ΔH_{vap}/kJ mol^{-1}	7.77	16.21	17.68	19.8
Dipole moment/Debye	1.98	1.03	0.78	0.38
Percentage ionic bonding	43	17	12	5
Solubility in water g/100 g of water at 273 K		82.3	221	234 at 283K

show no acid character when perfectly dry. In solution, HCl, HBr and HI are strong acids but HF is relatively weak (ionizes only 5%). This can be ascribed to strong electronegative nature of fluorine which makes its compounds highly stable. They are all polar covalent compounds. The polarity is maximum for HF and minimum for HI. At ordinary temperatures, HF molecules polymerize through hydrogen bonding Fig. 10·39.

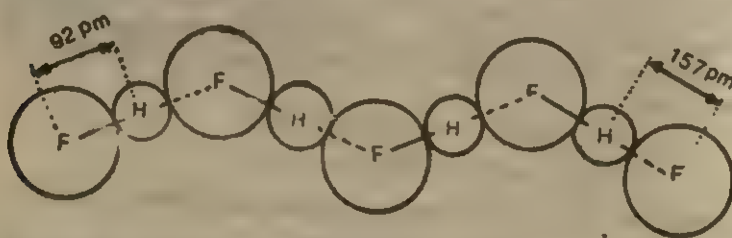


Fig. 10.39. Polymeric molecule of hydrogen fluoride resulting from hydrogen bonding.

Binary hydrides decompose when heated sufficiently. HI decomposes most easily while HF and HCl show only minor dissociation even at 1273 K. Thus, their thermal stability decreases as the formula mass increases. They fume in moist air and are soluble in water. In anhydrous state, they are almost inactive chemically and do not attack metals at ordinary temperatures.

Binary hydrides are covalent substances but their aqueous solutions conduct electricity. In aqueous solution, the H—X bond is broken and the proton becomes hydrated.

$$H{-}X(g)+H_2O(l) \longrightarrow H_3O^+(aq)+X^-(aq)$$

The heat of formation of H_3O^+ ion initiates the dissociation of bond. Since the bond in HI is the weakest, it ionizes strongly in solution. Thus acid strength decreases in the order HI > HBr > HCl > HF. Salts of these acids are called halides, the most important of which is NaCl.

Values of heats of formation and dissociation show a decrease in bond strength from HF to HI.

Of the four hydrides, HI is the most reducing agent. I^- is the most powerful electron donor. The reducing power of the hydrogen halides follows the sequence HI > HBr > HCl > HF. HF has no reducing properties. The highest bp, heat of formation and the bond energy and the lowest heat of vaporization of HF compared to other hydrides are ascribed to hydrogen bonding present in HF molecules.

Interhalogen compounds. The halogens combine with each other to give interhalogen compounds having the general formula,

AX_n(A = the central atom ; *n* is odd integer)

Their formation is ascribed to the small electronegative difference between the two halogen atoms. The compounds are prepared by the direct interaction of appropriate halogen under suitable conditions.

$$\underset{(1:1 \text{ ratio})}{I_2 + Cl_2} \longrightarrow 2ICl$$

$$Cl_2 + \underset{(\text{in excess})}{3F_2} \xrightarrow{553\text{ K}} 3ClF_3$$

Interhalogens are highly reactive substances. Their reactivity is better than the parent halogens (except fluorine) because their dissociation energy is less than halogens. They are covalent liquids or gases. They are good oxidising agents and are hydrolyzed easily. ClF_3 is an excellent fluorinating agent. Some of the compounds react with alkali metal halides and gives polyhalides.

$$KF + BrF_3 \longrightarrow K^+[BrF_4]^-$$

Both polyhalogen anions XY_{2n}^- (n=1, 2, 3, 4) and polyhalogen cations, (XY_{2n}^+) are known. Some other types of polyhalide ions, such as I_3^-, I_5^-, $IBrF^-$, $IFCl_2^-$ are also known. Conductivity measurement depicts a tendency of self-ionization among some interhalogens in liquid phase.

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

$$2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$

Some of the known interhalogens are listed below in Table 10.23.

TABLE 10.23 : Interhalogen compounds

Name	*AX*	*AX_3*	*AX_5*	*AX_7*
Fluorides	ClF(g)	ClF_3(g)	ClF_5	—
	BrF(l)	BrF_3(l), IF_3(l)	BrF_5(l), IF_5(l)	IF_7(g)
Chlorides	BrCl(g), ICl(s)	ICl_3(s)	—	—
Bromides	IBr(s)	(I_2Cl_6)	—	—

On the basis of VSEPR theory (Unit 6, Class XI textbook) and taking into account the lobes, unshared pair of electrons and bond piars, the possible geomety of some of the interhalogens and polyhalide ions are illustrated through Fig. 10.40.

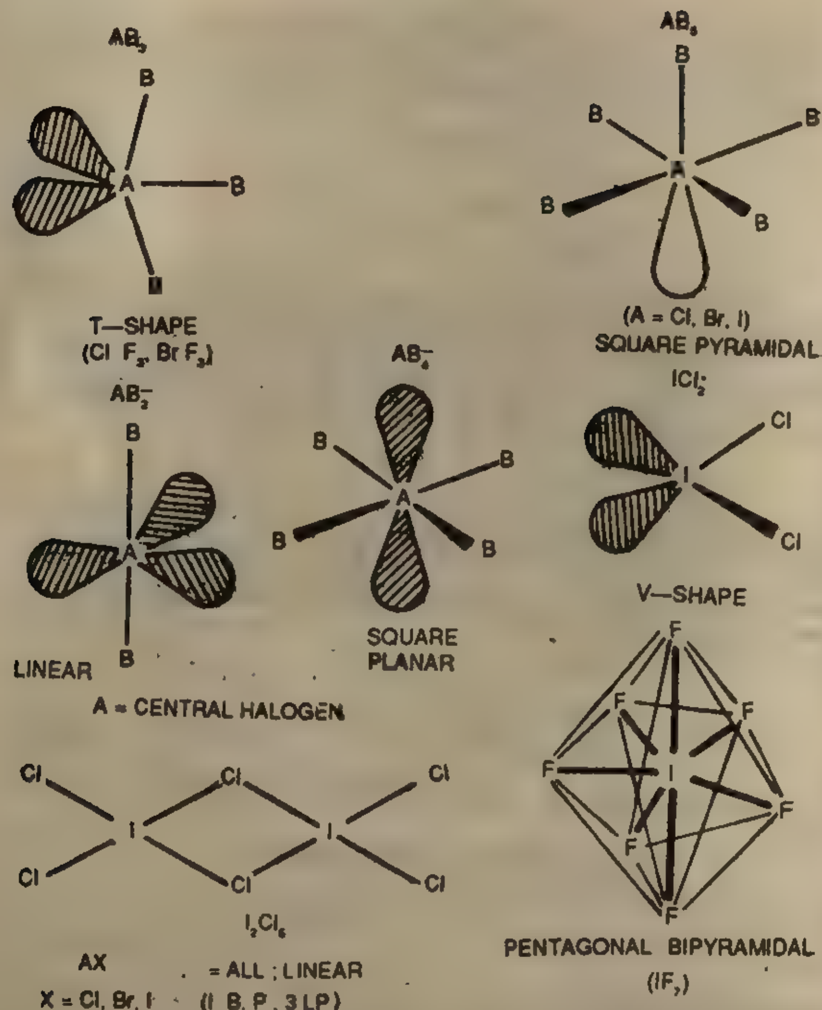


Fig. 10.40. Geometry of some interhalogen compounds and polyhalide ions.

10.10. GROUP 18 ELEMENTS : THE NOBLE GASES

The atmosphere contains a family of gaseous elements, the noble gases, which remained undiscovered on the earth until 1894. These gaseous elements, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) constitute the group 18 of the periodic table. Radon, the last and the radioactive member of the family is not present in the atmosphere.

These gases are collectively known by differents names, rare gases, inert gases or noble gases. The term inert is no longer applicable to the group as a whole because the heavier three members of the family (particularly xenon) are not inert. It is best to call them noble gases which would mean rightly their reluctance to react. You might recall at this moment the usage of the term noble to describe the chemistry of some metals such as gold, platinum, *etc.* Because of their low abundance on the earth, they have also been called rare gases.

All noble gases except helium have the stable outer electronic configurations $ns^2\,np^6$. Helium has the $1s^2$ configuration. The stable electronic configuration well explains for their high degree of chemical inertness in common chemical reactions. This configuration is also associated with inertness for ionized elements, *e.g.*, Na^+, Ca^{2+}, Al^{3+}, *etc.*, and is the basis of the 'octet rule'.

The unique chemical inertness associated with the name of the noble gases is reflected in the history of their discovery (Unit 13, class XI textbook) which was followed by a long gap of a few decades before xenon could be made to combine with only the most electronegative element fluorine.

All the noble gases are colourless, odourless and tasteless. They are all monoatomic in the gaseous state as suggested by the relatively high ionization energies. They remain gaseous at temperatures at which most of the other elements are liquids and solids.

Their boiling points, meltng points and heats of vaporization are extremely low. These properties indicate the absence of strong chemical bonds. Since all the valence electrons are paired in the ground state of the atom, only weak interatomic forces (van der Waals type) operate to hold the atoms together in the liquid and solid states. These forces arise because of the induction of a weak dipole in one electronic system by another. The increase in values (Table 10·24) with atomic mass points towards the increasing polarizability of the larger and diffuse electron clouds of the elements. Weak interatomic valence forces result in large atomic radii. Such radii are called **non-bonded van der Waals radii** and increase on descending the group as expected. These radii should never be misunderstood as covalent bonded radii.

The very stable electronic configuration of these elements gives them the highest ionization energy in each of their respective rows of the periodic table and consequently a low degree of chemical reactivity. With increasing atomic size there is a decrease in ionization energy (Fig. 10.41). It is relatively difficult to liquefy these gases as their atoms are held only by weak forces. The process of liquefaction becomes easier with increase in size as the van der Waals forces become stronger in nature The properties and the general trends in properties of the noble gases are summarized in

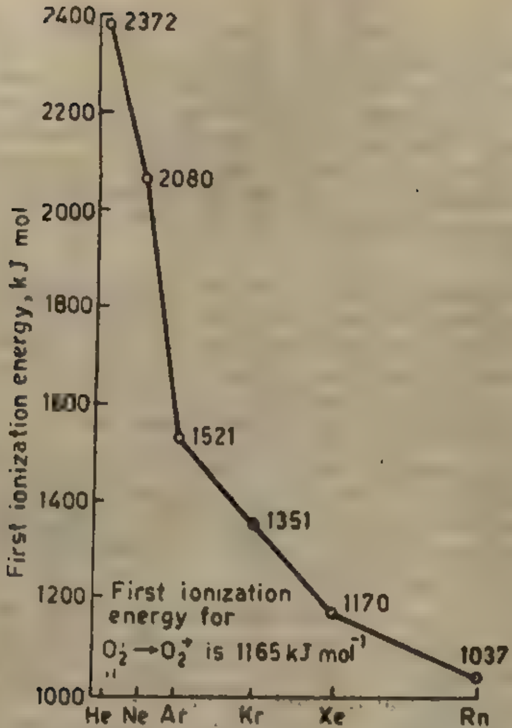


Fig. 10.41. Ionization energies of the noble gases.

Table 10.24. Helium is unique in some of its properties. When helium is cooled under one atmosphere pressure, it liquefies at

TABLE 10.24 : Some properties of the noble gases

Property	*He*	*Ne*	*Ar*	*Kr*	*Xe*	*Rn*
Atomic number	2	10	18	36	54	86
Outer shell electronic configuration	$1s^2$	$2s^2$ $2p^6$	$3s^2$ $3p^6$	$4p^6$ $4s^2$	$5p^2$ $5p^6$	$5s^2$ $6s^6$
First ionization energy IE/kJ mol^{-1}	2372	2080	1520	1351	1170	1037
Van der Waals radius, r/pm	140	154	188	202	216	—
Melting point, T/K	(a)	27	87	119.8	164	211
Boiling point, T/K	4.0	24.4	83.6	115.8	161	202
Heat of vaporization, ΔH_{vap}/kJ mol^{-1}	0.09	1.84	6.27	9.66	13.68	18.00
Abundance in dry air (ppm) by volume	5.24	18.18	93.40	1.14	0.087	Variable traces

(a) Helium is the only liquid which cannot be frozen by reducing temperature alone. Pressure must also be applied.

4.12 K. It acquires the normal properties of a liquid (helium-I) until it is cooled to 2.18 K. This liquid at 2.18K, with some abnormal characteristics, is called helium-II. It has been reffered to as the 'fourth state of matter'. The liquid is a superfluid, *i.e.*, its viscosity is almost zero and it can creep out of the vessel in which it is contained in defiance of gravity. It is unusually better conductor of heat and electricity than copper metal.

10.10.1. Chemistry of the Noble Gases

No real compounds of the noble gases were known until 1962. Since then rapid progress has been made in the field of noble gas compounds. Neil Bartlett (1962), in the course of his investigation of various reactions of fluorine with platinum and its salts in a glass apparatus, observed the formation of a red solid, $O_2^+ [PtF_6]^-$. The formation of this compound involves the loss of an electron from molecular oxygen.

$$O_2 + PtF_6 \longrightarrow O_2^+[PtF_6]^-$$

By the consideration that the first ionization energy of $O_2(O_2 \rightarrow O_2^+ + e^-)$ is close to the first ionization energy of xenon $(Xe \rightarrow Xe^+ + e^-)$, Bartlett reasoned that xenon might form a compound with PtF_6 similar to the dioxygenyl hexafluoroplatinate (V), $O_2^+ [PtF_6]^-$. In June 1962, he could actually prepare a yellow-red powder corresponding to $Xe^+[PtF_6^-]^-$ by interaction of PtF_6 with Xe.

$$Xe + PtF_6 \longrightarrow Xe^+[PtF_6]^-$$

This was the beginning of the research in an extremely challenging field of noble gas compounds. Since then many compounds have been isolated and characterized, *e.g.*, chemical compounds between fluorine and also oxygen and the noble gases krypton, xenon and radon. The compounds of krypton are fewer ; only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified by radiotracer techniques. No true compounds of Ar, Ne or He are known. This ability of compounds formation would be expected to increase with decreasing ionization energy. However, the chemical behaviour of xenon has drawn most attention and only the compounds of xenon will now be briefly described. Xenon forms a number of compounds with fluorine and oxygen. The best characterized fluorides of Xe are XeF_2, XeF_4 and XeF_6. The oxidation states of xenon in the compounds with fluorine and oxygen are +2, +4, +6, and +8. Figure 10.42 outlines the formation of the most important of these molecules.

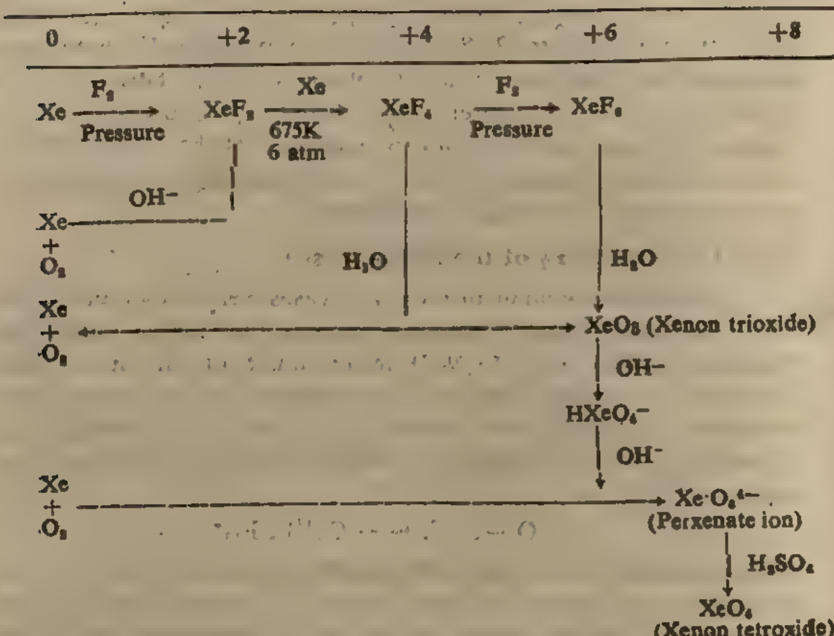


Fig. 10.42. *Outlines of the reactions leading to the formation of fluorine and oxygen compounds.*

The xenon fluoride, XeF_2, XeF_4 and XeF_6 are white crystalline solids at room temperature, melting at 402K, 362-373K and 322.6K respectively. XeF_6 is the most volatile (vapour pressure 25 mm at 298K). They are exothermic compounds. Each of the fluorides is prepared by direct interaction of Xe and F_2 in a sealed nickel or monel container. The product obtained depends on the temperature, pressure and mixing ratio of the elements.

XeF_2 :

$$\underset{(2:1 \text{ ratio})}{Xe+F_2} \xrightarrow[\text{pressure}]{675K,\ 2\ hr} XeF_2 \ (99.7\% \text{ yield})$$

The heated mixture is subsequently cooled. A white solid of XeF_2 separates on vacuum sublimation. Both XeF_4 (0.3%) and XeF_6 (negligible) are also formed.

XeF_2 can also be prepared by exposing the gas mixture to sunlight at one atmosphere pressure for a few hours. On exposing a mixture of Xe and OF_2 to sunlight, XeF_2 separates. Hydrolysis of XeF_2 yields xenon and oxygen. The hydrolysis is slow in dilute acid but rapid in basic solution.

$$XeF_2+2OH^- \longrightarrow Xe+\tfrac{1}{2}O_2+2F^-+H_2O$$

The pungent smelling solution of XeF_2 is a powerful oxidizing agent, *e.g.*, HCl gives Cl_2. XeF_2 acts as a mild fluorinating agent for organic compounds.

XeF_4 : Pure XeF_4 is difficult to prepare by the usual thermal methods. It usually separates together with XeF_2 and XeF_6. It is difficult to remove XeF_2 by fractional distillation (similar vapour pressure at room temperature). XeF_6 can be easily separated (discussed later).

Since XeF_6 is easily removed, so it is good to employ an excess of F_2 to reduce the formation of XeF_2.

$$\underset{(1:5 \text{ ratio})}{Xe+F_2} \xrightarrow[6 \text{ atm}]{675-775K} XeF_4$$

XeF_4 undergoes hydrolysis to oxides and oxoanions.

$$6XeF_4+12H_2O \longrightarrow 2XeO_3+4Xe+3O_2+24HF$$

$$XeO_3+OH^- \longrightarrow HXeO_4^-$$

It reacts with hydrogen to form Xe and HF. It is a potent oxidizing agent and fluorinates the ring in substituted arenes such as toluene.

XeF_6 : Synthesis of XeF_6 requires vigorous conditions.

$$\underset{(1:20 \text{ ratio})}{Xe+3F_2} \xrightarrow{573-675K,\ 10-20 \text{ hr},\ 50-200 \text{ atm}} XeF_6$$

A 95% yield is obtained together with impurities of the kind XeF_2, XeF_4 and $XeOF_4$.

XeF_6 reacts with quartz.

$$2XeF_6+SiO_2 \longrightarrow 2XeOF_4+SiF_4$$

Similar to XeF_4, it also get hydrolyzed.

$$XeF_6+3H_2O \longrightarrow XeO_3+6HF$$

Partial hydrolysis of XeF_6 gives the oxyfluorides $XeOF_4$ and XeO_2F_2.

Xenon fluorides react with fluoride ion acceptors yielding cationic species and fluoride ion donors to give fluoroanions :

$$XeF_2+PF_5 \longrightarrow [XeF]^+[PF_6]^-$$

$$XeF_4+SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$$

$$XeF_6+MF \longrightarrow M^+[XeF_7]^- \ (M=Na, K, Rb, Cs)$$

Purification of XeF_4 : XeF_4 remains contaminated with some of XeF_2 and XeF_6. It can be purified by making use of its inability to donate fluoride ion to AsF_5 acceptor. Impure XeF_4 is dissolved in BrF_5 and treated with an excess of AsF_5. XeF_2 and XeF_6

from non-volatile salts $[Xe_2F_3]^+[AsF_6]^-$ and $XeF_5^+AsF_6^-$ respectively. Unreacted BrF_5 and AsF_5 are distilled off at 273K. Pure XeF_4 is then obtained by vacuum distillation at room temperature.

$$\left.\begin{array}{l} XeF_2 \\ XeF_4 \\ XeF_6 \end{array}\right\} \xrightarrow[\text{excess } AsF_5]{\text{Dissolve in } BrF_5 \text{ and add}} \begin{array}{l} [Xe_2F_3]^+[AsF_6]^- + \text{unchanged} \\ XeF_4 + \text{unchanged } BrF_5 \\ \text{and } AsF_5 + [XeF_5]^+[AsF_6]^- \end{array}$$

$$\begin{array}{l} -AsF_5 \\ -BrF_5 \end{array} \Big\downarrow \begin{array}{l} \text{Distillation} \\ \text{at 273K} \end{array}$$

$$XeF_4 \xleftarrow[\text{at room temperature}]{\text{Vacuum sublimation}} [Xe_2F_3]^+[AsF_6]^- + XeF_4 + [XeF_5]^+[AsF_6]^-$$

XeF_6 can be further purified by taking advantage of its ability to form stable compounds with NaF. The impurities do not form stable complexes with NaF and can be pumped off at 325K. The stable complex $2NaF.XeF_6$ is then heated to 400K under vacuum when it gives pure XeF_6.

Compounds with Xe O bonds

Both XeF_4 and XeF_6 on hydrolysis give xenon trioxide (Table 10.25). It is a white deliquescent solid and is dangerously explosive. It is a powerful oxidizing agent in aqueous solution.

$$XeO_3 + 6H^+ + 9I^- \longrightarrow Xe + 3H_2O + 3I_3^-$$

Xenon tetraoxide is a highly unstable and explosive gas. It is obtained by the reaction of conc H_2SO_4 on barium perxenate.

Several oxofluorides are known, but the best characterized are $XeOF_4$ and XeO_2F_2

$$\underset{\text{(stoichiometric amount)}}{XeF_6 + H_2O} \longrightarrow XeOF_4 + 2HF$$

$$XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$$

$$2XeO_3 + XeF_6 \longrightarrow 3XeO_2F_2$$

$$XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4.$$

TABLE 10.25 : Group VIII oxides

Oxide	*Preparation*	*Comments*
XeO_3	$3XeF_4 + 6H_2O \rightarrow XeO_3 + 2Xe + 3/2\,O_2 + 12HF$ $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$	Dangerously explosive solid. In basic solutions gives $HXeO_4^-$, which disproportionates to give $XeO_6^{4-} + Xe + O_2$ triangular pyramidal structure.
XeO_4	$Ba_2XeO_6 \xrightarrow{H_2SO_4} XeO_4 + BaSO_4 + H_2O$	Unstable, explosive gas. Tetrahedral structure.

Structures of Xenon Fluorides and Oxofluorides

In the formation of XeF_2 one of the 5p electrons in Xe is uncoupled and promoted to the 5d orbital. The two unpaired electrons form bonds with two fluorine atoms. Thus Xe assumes sp^3d hybridization. Because of the presence of 3 lone pairs of electrons, the Xe and F atoms lie in a straight line (liner disposition).

In XeF_4, two of the 5p electrons are promoted to the 5d orbitals. In the process, Xe assumes sp^3d^2 hybridization. Because of the presence of two lone pairs, the molecule acquires a square planar structure.

In XeF_6, three 5p electrons are promoted to the 5d orbitals. In the process, Xe assumes sp^3d^3 hybridization. Because of the presence of one lone pair of electrons, the molecule acquires a distorted octahedron with a non-bonding electron pair extending either through face or through an edge.

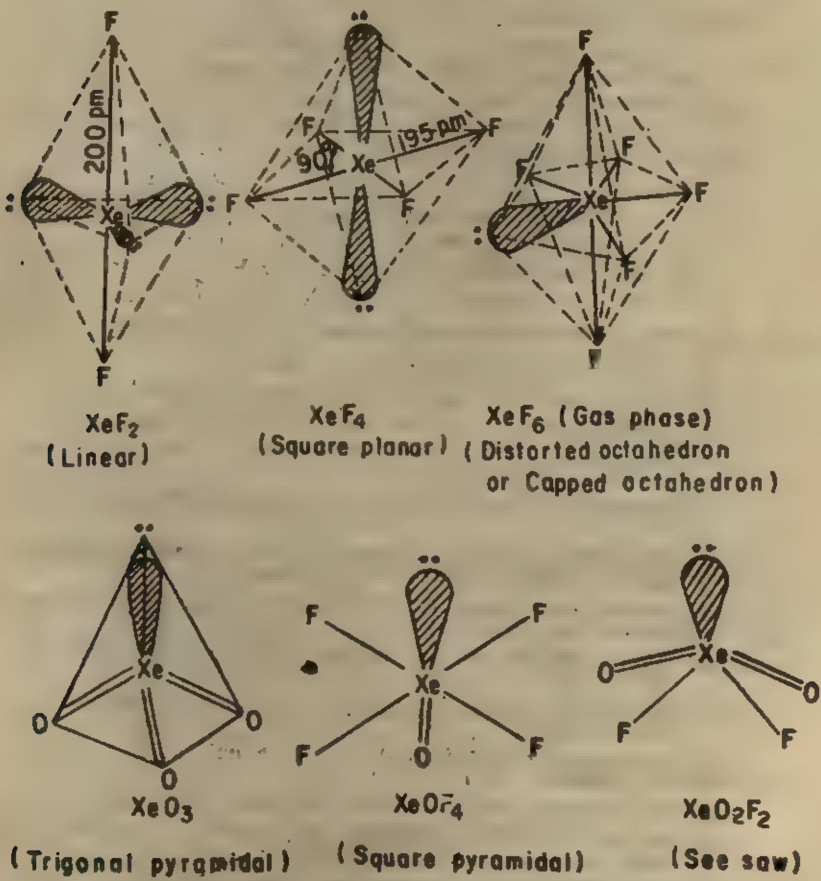


Fig. 10.43. Structures of xenon fluorides and oxofluorides.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

10.1. **Choose the correct answer of the four alternatives given for the following questions :**

(*i*) Which of the following metals is present in chlorophyll ?
(*a*) magnesium (*b*) iron (*c*) sodium (*d*) beryllium

(*ii*) Which of the following interhalogens does not exist ?
(*a*) ClF_3 (*b*) IF (*c*) ICl_3 (*d*) IF_4

(*iii*) Which of the following halogens is the strongest oxidizing agent ?
(*a*) fluorine (*b*) chlorine (*c*) bromine (*d*) iodine

(*iv*) Which of the following hydrohalic acids is the stronges acid ?
(*a*) HCl (*b*) HBr (*c*) HI (*d*) HF

(*v*) Only one oxygen atoms of two SiO_4 tetrahedra is shared in
(*a*) cyclic silicates (*b*) orthosilicates
(*c*) chain silicates (*d*) pyrosilicates

(*vi*) Carbon dioxide is
(*a*) an acidic oxide (*b*) a basic oxide
(*c*) an amphoteric oxide (*d*) a neutral oxide

(*vii*) Which of the following is reduced most readily ?
(*a*) iodine (*b*) chlorine (*c*) fluorine (*d*) bromine

(*viii*) The oxidation state of sulphur in H_2SO_4 is
(*a*) +2 (*b*) +4 (*c*) +6 (*d*) +8

(*ix*) Which of the following molecules assumes see-saw structure ?
(*a*) XeF_4 (*b*) XeO_2F_2 (*c*) $XeOF_4$ (*d*) XeF_2

(*x*) Which of the following oxides forms dimer ?
(*a*) NO (*b*) N_2O_3 (*c*) NO_2 (*d*) N_2O_5

10.2. **State which of the following statements are true (T) or false (F).**

(*i*) Peroxides contain oxygen in the −1 state.

(*ii*) Interhalogen compounds are strong reducing agents.

(*iii*) The spherical atoms of noble gases have very low polarity.

(*iv*) Radon, because of its higher ionization energy than xenon does not form compounds readily.

(*v*) Nitrogen, in its compounds, shows oxidation states from −3 to +5.

(*vi*) XeF_6, $XeOF_4$ and XeO_3 assume different structures but in all the three compounds Xe shows +6 oxidation state.

(*vii*) At room temperature, both nitrogen and phosphorus exist as diatomic molecules.

(*viii*) Bismuth usually shows only +3 oxidation state, and its hydroxide is basic.

(*ix*) The alkaline earth metals are somewhat more electropositive than the alkali metals.

(*x*) Aluminium hydroxide is amphoteric in nature.

10.3. **Fill in the blanks :**

(*i*) The electronic notation for $_{33}As$ is $1s^2, 2s^2, 2p^6$;————.

(*ii*) The most common compounds of silicon are the ———— of which many varieties occur as natural ————.

(*iii*) Boron, in each of its borate anions, is surrounded by ————

(*iv*) Mica mineral has the composition————.

(*v*) Tin (II) chloride crystallizes from concentrated acid solution as————.

(*vi*) The anhydride of orthophosphoric acid is ————.

(*vii*) The chemical inertness of nitrogen results from the ———— of N≡N bond.

(*viii*) XeF_2 molecule assumes ———— structure.

(*ix*) Oxides of chlorine are ———— and potentially ————.

(*x*) The —O—O— single bond is present in ionic and covalen——t.

TERMINAL QUESTIONS

10.1. (*i*) Which would you predict to have the higher ionization energy, H or H_2 ? Why ?

(*ii*) Explain how does hydrogen form both H^- ion and the H^+ ion.

10.2. (*i*) Give reasons why H_2 is seldom used as a commercial reducing agent for metal oxides.

(*ii*) Describe why the H^+ ion does not exist by itself in chemical systems.

10.3. Why do the group 1 elements (*a*) show metallic properties, and (*b*) commonly show only the +1 oxidation state in compounds ?

10.4. (*i*) How does hydrogen (*a*) resemble, and (*b*) differ from the halogens ?

(*ii*) In what ways is the chemistry of hydrogen similar to that of group 1 and in what ways does it differ ?

10.5. Explain the following statements :

(*i*) The first member of a group often shows anomalous properties. Give two facts in which the behaviour of Li is anomalous.

(*ii*) In a normal chemical reaction Na^+ is formed rather than the ion Na^{2+}.

(*iii*) Ionization energies are related to the reactivity of elements.

(*iv*) Mg^+ ion is not found in compounds even though less energy is required to remove one electron from Mg and from this ion than is required to remove two electrons to form Mg^{2+}.

(*v*) Group 2 elements frequently form hydrated salts, while the corresponding compounds of group 1 elements are anhydrous.

10.6. State how each of the following properties of the elements in groups 1 and 2 will change with increasing atomic number : (*i*) atomic radius, (*ii*) ionization energy, (*iii*) strength as reducing agents, (*iv*) electropositivity, and (*v*) hydration energy.

10.7. (*i*) Account for the fact that the alkaline earth metals are generally higher melting than the alkali metals.

(*ii*) Account for each of the following trends going down the group 2 from Be to Ba.

1. Hydroxides become more basic and soluble.
2. Sulphates become less soluble.
3. Carbonates become more stable with respect to thermal decomposition to form the oxide and CO_2.
4. The reduction potential values become more negative.

10.8. (*i*) Why is the first ionization energy of beryllium greater than that of lithium, while the second ionization energy of beryllium is less than that of lithium ?

(*ii*) Why is LiF less soluble than CsI and why is LiI more soluble than CsI ?

(*iii*) Why is the Be^{2+} the only group 2 metal ion that undergoes hydrolysis ?

10.9. (*i*) Explain why, although Na^+ and Mg^{2+} have the same electron structure, the radius of Mg^{2+} is only 72 pm.

(*ii*) Explain why CaO(s) has a higher standard lattice energy than $CaCO_3$(s).

10.10. What are an oxide, a peroxide and a superoxide ? Why do you think that, on burning, lithium forms an oxide, sodium peroxide and potassium a superoxide ?

10.11. (*a*) State the flame colours for Ca, Sr and Ba. Suggest why magnesium compounds fail to produce a visible 'flame' colour ?

(*b*) Comment on the hydrolysis of $BeCl_2$, $MgCl_2$ and $BaCl_2$.

(*c*) Alkaline earth metal ions show an increased tendency to form complex compounds, compared to alkali metal ions. Comment.

10.12. Write a brief description on the following compounds of Group 1 and 2 elements.

(*a*) oxides and hydroxides (*b*) carbonates (*c*) halides

10.13. Is it surprising that boron participates in three-centre two-electron bonds ? Why ? Describe and illustrate the bonding in the three-centre two-electron bonds of B_2H_6.

10.14. Discuss the trends in the following properties of the groups 13 to 18 elements :

(*a*) atomic radius, (*b*) ionization energy,
(*c*) electronegativity, and (*d*) structures of the oxides.

10.15. (*a*) Explain the term catenation and indicate its prevalence for the block elements.

(*b*) Discuss why BX_3 and AlX_3 (halides) are good electron acceptors.

10.16. (*a*) Discuss the reasons for the trends in the M—M bond strengths for C, Si, Ge, Sn and Pb.

(*b*) Beryl, a mineral, $Be_3Al_2Si_6O_{18}$ contains the discrete anion $Si_6O_{18}^{12-}$. Suggest the structure for the anion.

10.17. (*a*) Why is it not possible to obtain anhydrous aluminium chloride by heating the crystals of $AlCl_3 \cdot 6H_2O$?

(*b*) It is advisable to add a solution of NH_4OH to a solution of an aluminium salt to prepare $Al(OH)_3$, rather than to add a solution of NaOH. Comment.

10.18. (*i*) How does aluminium react with (*a*) chlorine, (*b*) HCl, and (*c*) NaOH ?

(*ii*) Why is solution of $Al_2(SO_4)_3 \cdot 12H_2O$ acidic ?

10.19. How is orthoboric acid obtained ? Why does an aqueous solution of boron turn red litmus blue ?

10.20. (*i*) Give three reactions in which boron exhibits non-metallic behaviour.

(*ii*) Explain how the structures of elemental boron and of diamond are related to their hardness.

10.21. (*i*) Compare boron and silicon with respect to atomic size, ionization energy, and electronegativity.

(*ii*) Explain why in many respects lithium is similar to magnesium, beryllium to aluminium, and boron to silicon.

10.22. Why is B_2H_6 said to be an 'electron deficient' compound ? Comment on the existence of BH_3 molecule.

10.23. (*i*) Why does aluminium resist oxidation by O_2 (except at high temperature) and HNO_3 ?

(*ii*) From aluminium to thallium, what is the change in (*a*) stability of M^{3+}, (*b*) electrode potential, (*c*) reactivity of M toward OH^-, and (*d*) oxidizing ability of M^{3+} ?

10.24. Account for the following observations :

(*a*) In trimethylamine, the nitrogen has a pyramidal geometry whereas in trisilylamine $N(SiH_3)_3$ it has a planar geometry.

(*b*) Elemental silicon does not form a graphite-like structure as carbon does.

10.25. What are silicones ? How are they manufactured ?

10.26. (*i*) Why is the melting point of boron so high ?

(*ii*) Which would you expect to be a better Lewis base : the carbide ion, C^{4-}, or the silicide ion, Si^{4-} ?

(*iii*) Contrast the properties of CO_2 and SiO_2.

10.27. Discuss and give equations for the hydrolysis of the halides, $SiCl_4$, SiF_4 and NF_3.

10.28. Suggest a method for the preparation of the oxides : Al_2O_3, SiO_2, NO, P_4O_{10}, SO_3, Cl_2O_7, ClO_2 and XeO_3.

10.29. Give the structures of the species listed below : CO_2, NO_2, XeF_4, BF_4^-, ICl_2^-, SF_4, PCl_5, SeO_2.

10.30. (*i*) Sn(II) is a better reducing agent in basic solution than in acidic solution. Explain.

(*ii*) Account for the fact that a fresh precipitate of $PbCl_2$ is soluble in excess HCl.

(*iii*) Account for the fact that a graphite-like form of silicon is not observed.

(*iv*) Silicon forms SiF_4 and $[SiF_6]^{2-}$ but carbon forms only CF_4. Explain.

(*v*) Although CF_4 is unreactive toward water, SiF_4 hydrolyzes rapidly. Explain.

10.31. How are the silicates classified ? Draw their structures.

10.32. (*i*) For group 14 elements simple ions (single element) with a charge of 4+ or 4− are rare. Comment.

(*ii*) Why are pure silicon and germanium good semiconducting elements ?

(*iii*) Explain on the basis of their electronic structures, why tin is metallic and carbon is non-metallic.

(*iv*) How does SiF_4 differ from $SiCl_4$ in its hydrolysis ?

10.33. Compare the elements of group 14 with respect to (*a*) the crystal structure of the element, (*b*) the thermal stability of the hydrides, (*c*) the stability to hydrolysis of the halides. (*d*) the oxidation states of the elements, and (*e*) the basicity of the oxides MO_2 and MO.

10.34. Give a comparative account of the chemistry of the elements of group 14 and of their principal compounds.

10.35. Comment on the following statements :

(*i*) The chemistry of carbon is dominated by the ability of the carbon atom to bond to itself and to form multiple bonds to itself and to other atoms.

(*ii*) The chemistry of silicon is dominated by the ability of silicon to form strong bonds to oxygen and to the reluctance of silicon to bond to itself.

10.36. Discuss with reference to group 14 elements :

(*i*) the relative thermal stability of the dichlorides and tetrachlorides.

(*ii*) the variation of acid/base character of the oxides MO, and MO_2 with increase in atomic number.

(*iii*) Tin and lead have variable oxidation states and form complex ions ? Why then are they not classed as transition metals ?

10.37. Compare the chemistry of nitrogen and phosphorus with respect to (*a*) the structure of the elements, (*b*) the hydrides (bonding, basicity, thermal stability and reaction with oxygen), and (c) the chlorides (preparation, bonding and reaction with water).

10.38. What is the reason for the large difference in reactivity between N and P ? What similarities justify the inclusion of the two elements in the same group of the periodic table ?

10.39. (*i*) Explain why nitrogen can form N^{3-} ions but arsenic cannot form As^{3-} ions.

(*ii*) Which of the hydrides, NH_3 and PH_3, is the stronger base ? Explain.

(*iii*) Arrange the following in the decreasing order of property indicated :

(*a*) F_2, Cl_2, Br_2, I_2—bond energy

(*b*) HF, HCl, HBr, HI—acid strength (in water)

(*c*) M—F, M—C, M—Br, M—I—ionic character of the bond

(*d*) ClO_4^-, BrO_4^-, IO_4^-—oxidizing power

10.40. Account for the following observations :

(*i*) Molecular nitrogen N_2 is not particularly reactive.

(*ii*) H_3PO_3 is diprotic.

(*iii*) Nitrogen forms no pentahalides unlike phosphorus.

(*iv*) Water has a higher boiling point than H_2S.

10.41. Describe with explanations, the structures of $PCl_5(g)$, $PCl_5(s)$, $POCl_3$, NH_2^- and N_3^-.

10.42. (*i*) Why are compounds containing N—N bonds uncommon ?

(*ii*) The stability to heat of the hydrides, their reducing power and their basic strength all decrease in the order

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. Explain.

(*iii*) The basicity of the group 15 oxides increases down the group. Explain.

10.43. (*i*) Arrange the following oxides of nitrogen according to increasing oxidation state of nitrogen : N_2O_5, NO, NO_2, N_2O_4, N_2O_3, N_2O.

(*ii*) Explain why nitrogen forms only NCl_3 but phosphorus can form both PCl_3 and PCl_5.

(*iii*) Compare the acid strength of (*a*) HNO_3 and HNO_2, and (*b*) H_3PO_4 and HNO_3.

(*iv*) Suggest a reason for the fact that when Cu reduces conc. HNO_3, NO_2 is formed, while with dilute HNO_3, NO is the product.

10.44. List the elements in group 16 of the periodic table in order of increasing (*a*) atomic number, (*b*) melting point, (*c*) electronegativity, and (*d*) strength as oxidizing agent.

10.45. Halogens form various types of compounds with oxygen. Is it justified to call them the halides of oxygen ?

10.46. (*a*) How do you account for the high viscosity and high boiling point of concentrated H_2SO_4 ?

(*b*) What types of hybridizations of sulphur atom assumed in the following ions and molecules ?

SO_4^{2-}, SO_2, SO_3, SO_3^{2-}

Also mention the oxidation state of sulphur in each.

10.47. Comment on the structural features :

(*a*) Both SO_2 and SO_3 molecules assume sp^2 hybridization. SO_2 is angular while SO_3 is trigonal in shapes.

(*b*) Ozone has resonating structures.

(*c*) SO_4^{2-} ion is tetrahedral.

(*d*) Sulphur is S_8 while oxygen is O_2.

(*e*) The O—O bond energy in O_2 is much larger than the S—S bond energy in S_8.

10.48. Arrange H_2X (X = O, S, Se, Te, Po) compounds in order of increasing (*i*) acidity, (*ii*) hydrogen bonding, (*iii*) stability, and (*iv*) reducing power. Explain your conclusions.

10.49. Expiain the following :

(*i*) H_2S is a better reducing agent than H_2O.

(*ii*) All the bond lengths for S—O present in H_2SO_4 are equal.

(*iii*) H_2SO_4 is added to water while making a dilute solution of H_2SO_4.

(*iv*) The concentrated and hot H_2SO_4 is a better oxidizing agent than dilute and hot H_2SO_4.

10.50. State reasons for the following :

(*i*) H_2S is a gas at ordinary temperatures whereas H_2O is a liquid.

(*ii*) Oxygen is a stronger oxidizing agent than S, Se, *etc.*

(*iii*) H_2Te and H_2Se are better reducing agents than H_2.

(*iv*) Oxygen usually does not exhibit +2, +4 and +6 oxidation states in its compounds.

(*v*) The heat is evolved when concentrated H_2SO_4 is added to water.

10.51. (*a*) Explain the absence of positive oxidation states for oxygen.
(*b*) Sulphites are good reducing agents Explain.
(*c*) Why does conc. H_2SO_4 decolourize blue copper sulphate crystals ?
(*d*) The boiling points of CH_4, NH_3, H_2O and HF are 113K, 240K, 373K and 292K respectively. Explain the maximum value for H_2O.

10.52. Give the structural formulae for the following : (*i*) SF_6, (*ii*) H_2SO_4, (*iii*) SO_3^{2-} ion, and (*iv*) SO_3.

10.53. Discuss the general trend in the characteristics of the elements of group 16 with reference to (*a*) electronic configuration, (*b*) electronegativity, (*c*) catenation, (*d*) melting and boiling points, and (*e*) structures of elements.

10.54. (*a*) Oxygen shows mainly electrovalency while sulphur shows covalency in its compounds. Comment.
(*b*) A measure of the industrialization of a country is the consumption of sulphuric acid. Comment.
(Hint) : (*a*) Since sulphur is a larger and less electronegative atom than oxygen, its compounds have a higher degree of covalency.

10.55. (*i*) Discuss the difference between basic and acidic oxides.
(*ii*) How do the structures of oxides relate to their chemica properties.

10.56. (*i*) Explain why the reaction $O^-(g) + e^- \longrightarrow O^{2-}(g)$ is strongly endothermic while the reaction $O(g) + e^- \longrightarrow O^-(g)$ is exothermic.
(*ii*) Why are compounds containing S—S bonds more stable than compounds containing O—O or Se—Se bonds ?

10.57. Which member of each of the following pairs is the more acidic oxide ?
(*a*) BaO and CO_2 (*b*) NO and N_2O_5 (*c*) SO_3 and SeO_3
(*d*) ClO_2 and Cl_2O

10.58. Name the anhydrides of the following acids :
$HClO_4$, $HBrO_3$, $HClO_3$ and HIO_3
Which are the strongest oxidizing and the reducing agents ? Give reasons in support.

10.59. Arrange the halogens in order of decreasing : (*a*) ionization potential, (*b*) oxidizing power, (*c*) bond energy, (*d*) atomic radius, (*e*) electronegativity, (*f*) boiling point, and (*g*) intensity of colour.

10.60. Explain the following with reasons :
(*a*) Is aqueous solution of iodine brown ?
(*b*) Hydrogen bonding affect the properties like heat of vaporization, boiling point, *etc.*
(*c*) OF_2 is called oxygen fluoride rather than fluorine oxide.
(*d*) The strength of the following acids decreases in the order :
$HClO_4 > HClO_3 > HClO_2 > HClO$
(*e*) Fluorine is more reactive than other halogens.
(*f*) Among hydrohalides, HF is the least volatile and HCl is the most volatile.
(*g*) Chlorine, bromine and iodine show higher oxidation states than fluorine.

(*h*) HF is the weakest acid amongst hydrohalic acids (HF, HCl, HBr and HI).

(*i*) Iodine is more soluble in KI solution than in water.

(*j*) Interhalogens are more reactive than halogens.

10.61. From each of the sets given below, choose the compound which best serves the requirement specified :

(*i*) Most covalent : HF, HCl, HBr, HI

(*ii*) Most stable : HF, HCl, HBr, HI

(*iii*) Highest bp : F_2, Cl_2, Br_2, I_2

(*iv*) Most soluble in H_2O : F_2, Cl_2, Br_2, I_2

(*v*) Most industrially important : F_2, Cl_2, Br_2, I_2

(*vi*) Highest oxidation state of Cl : HCl, $HClO_2$, Cl_2O_7, $NaClO_4$

(*vii*) Most volatile : HF, HCl, HBr, HI

10.62. Arrange the hydrides of halogens with reasons in an increasing order of : (*i*) heat of vaporization, (*ii*) bond energy, (*iii*) ionic character, (*iv*) dipole moment, (*v*) reducing power, (*vi*) acid strength, and (*vii*) heat of formation.

10.63. (*a*) Mention the ways in which halogens can acquire noble gas configurations during compound formation.

(*b*) Give the various reactions of water and hydrogen with halogens.

10.64. Write short notes on : (*a*) Interhalogens, and (*b*) Polyhalides. What is unusual about fluorine ?

10.65. (*i*) The reaction of chlorine with water is one of the auto-oxidation-reduction reactions. Indicate the oxidation state changes.

(*ii*) Give a brief resume of the ways in which the behaviour of fluorine differs from the other halogens Name the factors responsible for the differences.

(*iii*) How do halogens react with NaOH solution (cold and hot) ?

10.66. (*a*) Generally halohalic acids are prepared by the action of concentrated sulphuric acid on the appropriate halides. But the method is not suitable for the preparation of HBr and HI. Explain.

(*b*) Why does HF tend to associate into bigger molecules ? Name two other compounds which also show association. Does association affect the properties of a molecule ? Explain the effects observed with HF in comparison to other compounds—HCl, HBr and HI.

10.67. Why do the oxyacids of halogens belong to a class of good oxidizing agents ? Is this also true of hydrohalic acids (HF, HCl, *etc.*) ? Give reasons.

10.68. List some common family characteristics of halogens.

10.69. What determines the strength of an acid ? How does strength differ from stability ?

10.70. Give a brief account of oxygen compounds formed with halogens.

10.71. (*i*) Why is the electron affinity of F less than that of Cl and why is the F—F bond weaker than the Cl—Cl bond ?

10.72. Determine and discuss the shapes of the interhalogen species ClF_3, IF_5, ICl_4^- and BrF_2^+.

10.73. Which of the following statements are correct ?

(*a*) Helium was the first noble gas to be discovered.

(*b*) It is no more justified to call them rare gases.

(*c*) Radon is one of the constituents of the atmosphere.

(*d*) Van der Waals radii of noble gases are smaller than atomic radii.

(*e*) Noble gases are diatomic in the gaseous state.

(*f*) Strong chemical bonds exist in the liquid and solid states of noble gases.

(*g*) Helium does not represent a completed shell.

(*h*) Noble gases have higher ionization potentials than those of any other elements in their respective horizontal rows of the periodic table.

10.74. (*i*) What is unusual about helium below 2.18 K ?

(*ii*) Which of the noble gases are capable of forming compounds ? Write formulae to illustrate some of these compounds.

10.75. (*i*) Explain the chemical inactivity of the noble gases.

(*ii*) Xenon shows more tendency to form compounds than other family members. Explain.

10.76. (*i*) Why were the first successful attempts at preparing compounds of xenon made with fluorine ?

(*ii*) In what ways do the boiling and melting points of the noble gases behave with increasing size of the gas ? Explain.

(*iii*) Give reasons for the low boiling points of the noble gases.

10.77. Discuss the discovery of the noble gases. Why did they remain undiscovered for such a long time ?

10.78. (*i*) Light noble gases, He and Ne are not capable of forming many compounds. Explain ?

(Hint) : Higher ionization potential than Xe.

(*ii*) Give a detailed method for the preparation of pure XeF_4.

10.79. Write short notes on :

(*a*) Van der Waals forces in noble gases.

(*b*) Unique properties of helium.

(*c*) Structures of xenon fluorides.

10.80. Predict the structures for each of the following on the basis of VSEPR theory :

XeF_2^+, XeO_3, XeF_5^+, XeF_6^{2+}, XeF_4

10.81. (*i*) XeO_3 is a powerful oxidizing agent. In acid solution it is reduced to Xe as it oxidizes Cl^- to Cl_2 abd Br^- to BrO_3^-. Give balanced equations for these reactions.

(*ii*) Suggest a method for the preparation of each : XeF_4, XeO_3, XeF_2 and $HXeO_4^-$.

ANSWERS TO SELF ASSESSMENT QUESTIONS

10.1. (*i*) (a) (*ii*) (b) (*iii*) (a) (*iv*) (c) (*v*) (d)
(*vi*) (a) (*vii*) (c) (*viii*) (c) (*ix*) (b) (*x*) (c)

10.1. (*i*) T (*ii*) F (*iii*) T (*iv*) F (*v*) T
(*vi*) T (*vii*) F (*viii*) T (*ix*) F (*x*) T

10.3. (*i*) $3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$ (*ii*) silicates, minerals
(*iii*) three oxygen atoms (*iv*) $K_2O.3Al_2O_3.6SiO_2.2H_2O$
(*v*) $SnCl_2.2H_2O$ (*vi*) phosphorus pentoxide
(*vii*) high bond energy (*viii*) linear
(*ix*) unstable, explosive (*x*) peroxides

□ □

UNIT 11

Transition Metals Including Lanthanides

Who knows not their sense
(These elements),
Their properties
And power not sees,
No mastery he inherits
Over the spirits.

J.W. VON GOETHE (1808)

UNIT PREVIEW

11.1 Introduction
11.2 General characteristics of transition elements and periodic trends.
11.3 General properties of first row transition metal compounds.
11.4 Differences between the first and the subsequent series of transition elements.
11.5 General chemistry of d-block elements and group trends.
11.6 Some important compounds.
11.7 Inner transition elements.
Self assessment questions.
Terminal questions.
Answers to self assessment questions.

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. State why the d-block and f-block elements can be described as transition and inner transition elements.
2. Characterize the elements on the basis of their typical properties.
3. Describe the general nature of transition metal compounds in regard to maximum oxidation state and most stable oxidation state, and relate the changes in oxidation-reduction character and in acidity-basicity with change of oxidation state.
4. State the common oxidation states of Cr, Mn, Fe, Cu, Ag, Zn, *etc.*, the compounds in which these oxidation states are represented, and the general nature of these compounds.

5. Characterize the f-blocks elements on the basis of their typical properties.
6. Compare the properties of first row transition elements with those of second and third rows transition elements.
7. State the cause of lanthanide contraction and its effect on the properties of lanthanides and elements in the 4d and 5d transition series.
8. State the points of differences between transition and inner transition elements and also between lanthanides and actinides.

11.1. INTRODUCTION

The term 'transition elements' was initially introduced to represent the elements in the middle of the periodic table that provide transition between the 'base formers' on the left and the 'acid formers' on the right. It applies to both the d-block and f-block elements all of which are metals. But we generally use the term **transition metals** for the metals which correspond to the filling of 3d, 4d, 5d and 6d sets of orbitals. The metals which correspond to the filling of 4f and 5f sets of orbitals are usually called the **inner transition metals**.

The transition and inner transition elements consist of the four series (Fig. 11.1). The first two series constitute exclusively transition elements. The third and fourth series, in addition to inner transition elements also contain transition elements (La, from Hf to Hg, Ac and Ku or Rf onward). The elements of the first series differ in a number of respects from the second and third series transition metals, which have closely similar chemistry.

In transition elements, the number of electrons in the occupied shell of the highest principal quantum number mostly remains constant while a penultimate shell is progressively filled up as the atomic number increases. Thus, atoms or ions of these elements contain incomplete d subshell, *i.e.*, 3d, 4d, 5d and 6d. They have the general electronic configuration $(n-1)\,d^{1-10}\,ns^{0\text{ to }2}$.

Transition elements of a given series behave much alike and resemble the elements of another periodic family. Although they appear in different periodic groups, their outer shells, with an occasional exception, contain the same number of electrons.

Zinc, cadmium, mercury have completely filled sets of d orbitals, and therefore, are not really d transition metals. However, they are often discussed with them because of the similarities of their properties to those of the transition metals. Copper, silver and gold also have completely filled sets of d orbitals. However, their cations have only partially unfilled sets of d orbitals.

Some of the general properties of the first row transition metals are smmarized in Tables 11.1 and 11.2. They are typical metals with high melting points and high heats of vaporization (or atomization), suggesting strong metallic bonding. This is due to the large number of valence electrons available for metallic bonding.

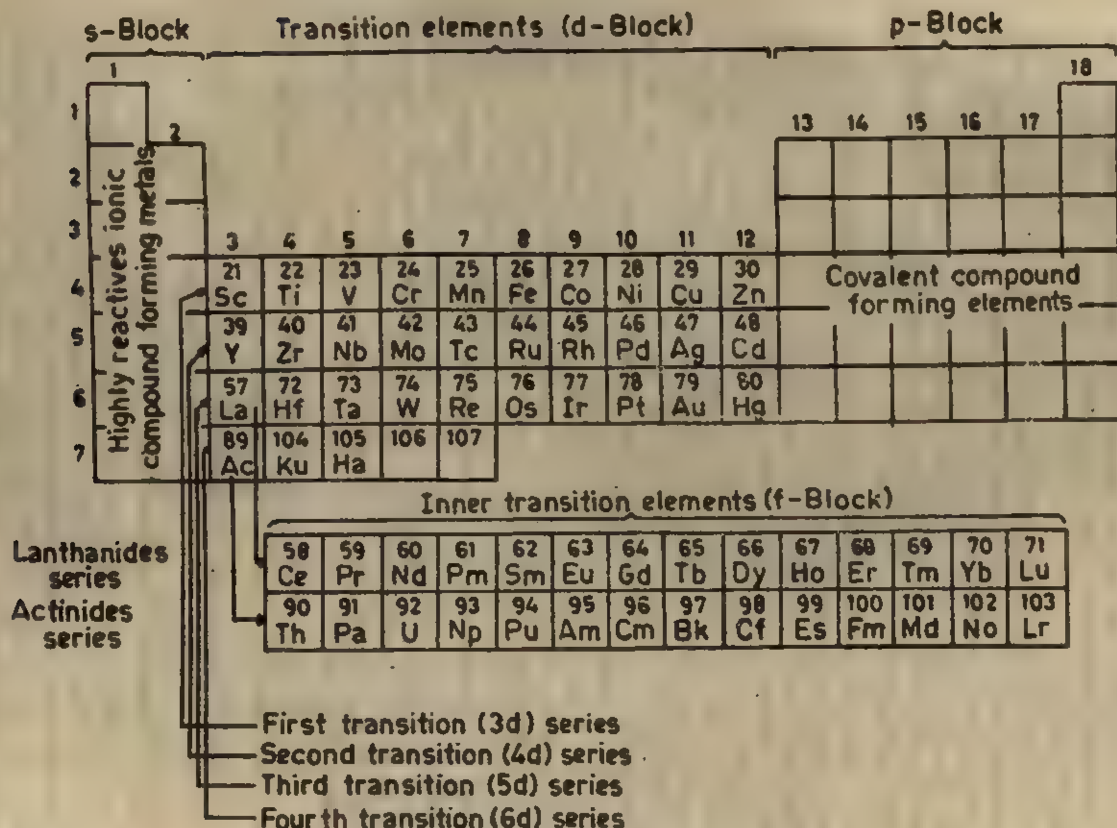


Fig. 11.1. Four series of transition elements.

Transition elements with partly filled d orbitals exhibit several interesting properties. For example, they display a variety of oxidation states, form coloured ions and enter into complex formation with different anions and neutral molecules. Many of the transition metals and their compounds possess the property of paramagnetism.

Striking similarities (horizontal and vertical) in successive members of the transition series are also observed. This is because of the fact that electrons enter an incomplete inner shell in building up the atom, while the outer level remains almost unchanged. The structural similarities and size give each transition group of elements their marked similarity of properties.

The physical and chemical properties of these metals cover a wide range and account for the large variety of their uses. Some of these metals are very hard and strong and are used as structural metals either in the pure state or as alloys. Most of the common materials around us : kitchenware, bicycles, automobile parts, railway lines, jewellery, *etc.* contain one or more of these transition metals. Many of the metals and their compounds find use as catalyst in chemical industries. Materials of future technology, *e.g.*, superconductors, are derived from compounds of the transition elements. Several of these metals are important as trace elements in living systems. Iron was the first trace element shown to be essential in the human diet. It is a component of haemoglobin. Additional trace metals hane been found to be essential to human nutrition : Cu, Mn, Zn, Co, Mo and Cr. Cobalt is a component of vitamin B_{12}. Both manganese and molybdenum are involved in formation of enzymes. Chromium is useful for glucose metabolism. Zinc is present in some of the enzymes and in the hormone insulin. Copper is involved in absorption and mobilization of iron required for haemoglobin. Metals form an important component of the mineral wealth of a country.

In this unit, we will deal with the characteristic properties of transition metals including lanthanides and actinides.

11.2 GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS AND PERIODIC TRENDS

11.2.1 Electronic Configuration

Transition metals have the general electronic configuration $(n-1)\ d^{1-10}\ ns^{0-2}$ where $(n-1)$ represents the penultimate shell. Their electronic configurations are given in Table 11.1. Irregular structures are found for chromium and copper because of the greater stability associated with half-filled and completely filled d orbitals. Similar irregularities are found in the second and third transition series.

The 4s orbital fills before the 3d as a consequence of orbital penetration as discussed in Unit 1. Thus, the $(n-1)$ d and ns energy

TABLE 11.1. Electronic configuration of the transition elements

First transition series (3d series)				Second transition series (4d series)				Third transition series (5d series)				Fourth transition series (Incomplete) (6d series)		
Element	Atomic number	Electronic configuration	Number of unpaired 3d electrons + 4s electrons	Element	Atomic number	Electronic configuration	Number of unpaired 4d electrons + 5s electrons	Element	Atomic number	Electronic configuration	Number of unpaired 5d electrons + 6s electrons	Element	Atomic number	Electronic configuration
Sc	21	$[Ar]3d^1 4s^2$	3	Y	39	$[Kr]4d^1 5s^2$	3	La	57	$[Xe]5d^1 6s^2$	3	Ac	89	$[Rn]6d^1 7s^2$
Ti	22	$-3d^2 4s^2$	4	Zr	40	$-4d^2 5s^2$	4	Hf	72	$-4f^{14} 5d^2 6s^2$	4	Ku	104	$[Rn]5f^{14} 6d^2 7s^2$
V	23	$-3d^3 4s^2$	5	Nb	41	$-4d^4 5s^1$	5	Ta	73	$-4f^{14} 5d^3 6s^2$	5			
Cr	24	$-3d^5 4s^1$	6	Mo	42	$-4d^5 5s^1$	6	W	74	$-4f^{14} 5d^4 6s^2$	6			
Mn	25	$-3d^5 4s^2$	7	Tc	43	$-4d^5 5s^2$	7	Re	75	$-4f^{14} 5d^5 6s^2$	7			
Fe	26	$-3d^6 4s^2$	6	Ru	44	$-4d^7 5s^1$	4	Os	76	$-4f^{14} 5d^6 6s^2$	6			
Co	27	$-3d^7 4s^2$	5	Rh	45	$-4d^8 5s^1$	3	Ir	77	$-4f^{14} 5d^7 6s^2$	5			
Ni	28	$-3d^8 3s^2$	4	Pd	46	$-4d^{10}$	1 or 2	Pt	78	$-4f^{14} 5d^9 6s^1$	2			
Cu	29	$-3d^{10} 4s^1$	1 or 3	Ag	47	$-4d^{10} 5s^1$	1	Au	79	$-4f^{14} 5d^{10} 6s^1$	1 or 3			
Zn	30	$-3d^{10} 4s^2$	2	Cd	48	$-4d^{10} 5s^2$	2	Hg	80	$-4f^{14} 5d^{10} 6s^2$	2			

levels lie close, so that the ns^1 electrons are not at significantly higher energy levels than the $(n-1)$ d electrons (Fig. 11.2).

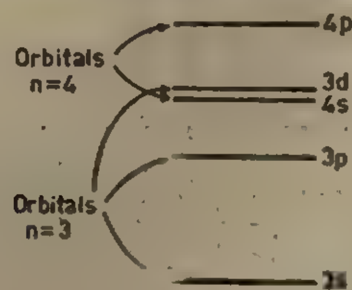


Fig. 11.2. Relative energy levels of the 3s, 3p, 3d, 4s and 4p orbitals. 3d orbital is 'on average' nearer the nucleus than 4s orbital, but at a higher energy level.

11.2.2. Physical Properties

Some of the physical properties of the first row transition metals are listed in Table 11.2. Their properties vary somewhat more irregularly with respect to position in the periodic table than do those of the representative elements. Vertical similarities are expected, of course, because of electron structural likeness.

There is a gradual decrease in **atomic radius** (Fig. 11.3). This is because the *n*d electrons, that are added to the atom, shield the outer *n*s electrons effectively from the increasing nuclear charge, and therefore, decreases in size are minimal. The radii of the elements at the end of the series increase as the increases in effective nuclear charge are outweighed by greater repulsions among d electrons in a given set of d orbitals. The transition metals of the

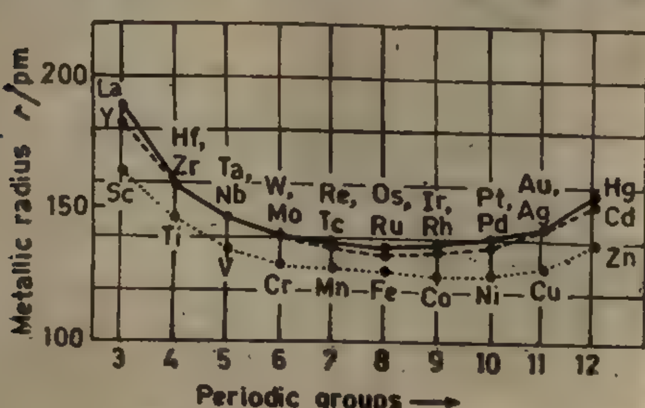


Fig. 11.3. Metallic radii of the transition metals

TABLE 11.2 : Some properties of the transition elements of first series (3d)

Element	*Metallic radius, r*/pm	*Ionization energy, IE*/kJ mol^{-1} *First*	*Second*	*Electro-negativity*	*Density at 293* K ρ/g cm^{-3}	*mp* T/K	*bp* T/K	*Electrode potential at 298* K, E°/V $M^{2+}(aq)+2e^- \rightarrow M(s)$
Sc	162	632	1240	1.3	3.00	1812	3015	—2.08
Ti	147	660	1310	1.50	4.50	1940	3558	—1.63
V	136	651	1410	1.60	6.10	2188	3623	—1.20
Cr	128	653	1590	1.88	7.9	2173	2963	—0.91
Mn	127	718	1508	2.07	7.2	1517	2333	—1.18
Fe	126	763	1560	2.10	7.86	1808	3023	—0.44
Co	125	760	1645	2.10	8.70	1768	3373	—0.28
Ni	124	737	1750	2.10	8.90	1728	3193	—0.25
Cu	128	746	1959	2.60	8.92	1356	2843	+0.34
Zn	138	907	1700	2.84	7.14	692	1180	—0.76

4d series have larger radii than those of the 3d elements. But the transition metals of the 5d series have nearly the same radii as the metals above them because of lanthanide contraction (to be discussed later).

The radii of bivalent metal ions also decrease across the period with increase in nuclear charge.

Ion	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
$r_{M^{2+}}$/pm	90	88	84	80	76	74	72	69

Most of the transition metals have a close packed structure in which each atom has tweleve nearest neighbours. The double effect of close packing and small atomic size results in strong metallic bonds between them.

Further with d electrons as well as s electrons available to take part in delocalization the metallic bond is strong in these metals. Hence, the transition metals have higher melting and boiling points, higher densities, higher heat of vaporization and smaller atomic volumes than s-block metals. Their strong interatomic bonding also explains their high tensile strengths and good mechanical properties.

Figure 11.4 shows how melting and boiling temperatures drop at manganese. In manganese, the d orbital is half-full. This arrangement appears to limit the availability of d electrons for delocalization.

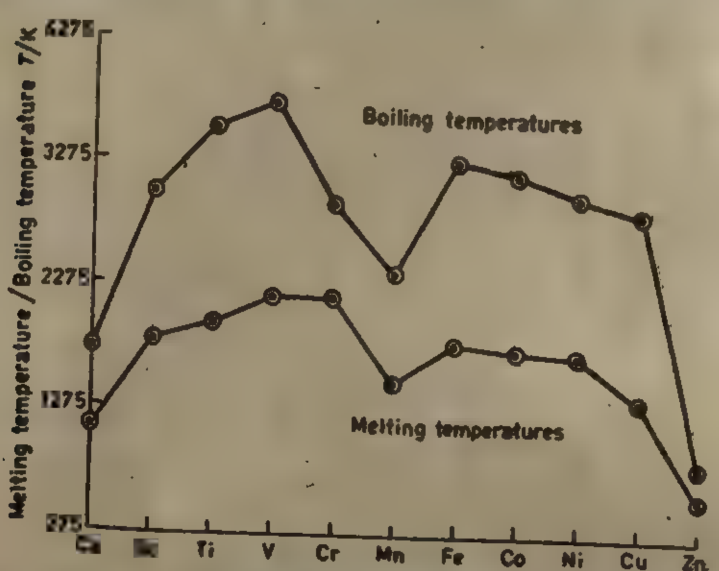


Fig. 11.4. Boiling and melting temperatures of 3d transition metals

The melting and boiling points of the elements of the first transition series are comparatively lower than the corresponding ones in the second and third transition series.

All elements have fairly high densities (Fig. 11.5). The high values of densities are correlated to high atomic masses, small atomic volumes and close packing. Within a group the density increases going down the group. Metals in second and third series have more protons and neutrons but almost the same atomic volume. The third series metals are very dense (Fig. 11.5) because of the lanthanide contraction.

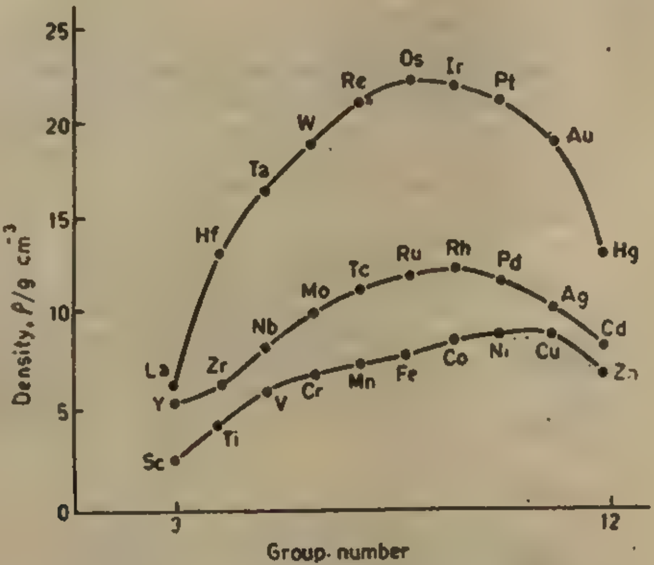


Fig. 11.5. Comparison of the densities of the transition metals of 3d, 4d *and* 5d *series.*

The gradual decrease in size along a period is accompanied by a gradual increase in ionization energy. In each period, there is a general increase owing to the increase in effective nuclear charge despite the screening effect provided by $(n-1)$ d level electrons. Plotted in Fig. 11.6 are the second ionization energies for each element in the transition metal series. Irregularities in the trend for the second ionization energies of Cr and Cu relate to the half-filled and completely filled d^5 and d^{10} orbitals respectively.

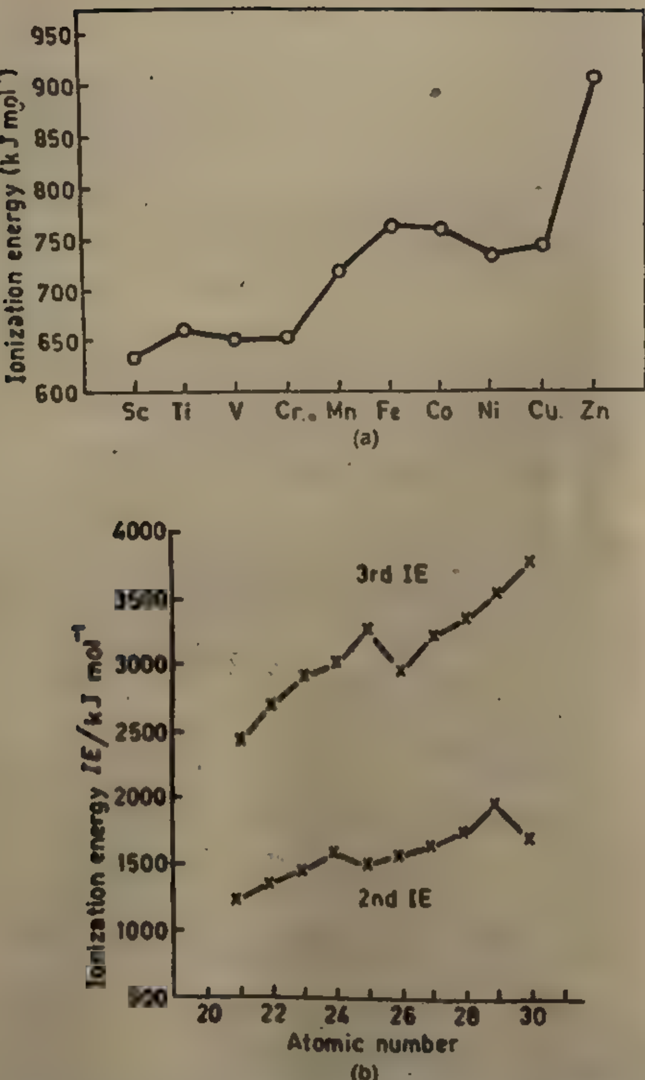


Fig. 11.6. The variation of the (a) first, and (b) second and third ionization energy with atomic number across the first series of transition metals.

11.2.3. Chemical Properties

The transition metals are all metals and show a gradual decrease in electropositive character upto the elements of copper

group. They are less electropositive than the s-block metals. Their electrode potentials indicate that all of them except copper should react with dilute solutions of strong acids (*e.g.*, HCl) to produce hydrogen gas. In practice, however, many of the metals react only slowly with dilute acids because of their surfaces being covered with inert, and insoluble layer of oxide. They also do not react, with common gases or liquids (hydrogen, oxygen, water, halogens, *etc.*).

Variable Oxidation States

Transition elements exhibit a wide range of oxidation states (Table 11·3), differing usually by units of one. This is because of the fact that $(n-1)$ d electrons may be involved along with ns electrons in bonding as electrons in $(n-1)$ d orbitals are in a comparable energy state to ns electrons (Fig. 11.2).

The following generalizations emerge from a study of the oxidation states of transition metals (3d series).

(*i*) The common oxidation states for each element include $+2$ or $+3$ or both. The $+3$ states are more common at the beginning of each series, whereas $+2$ states are more common towards the end.

(*ii*) From Sc to Mn the maximum oxidation state correlates with the total number of ns and $(n-1)$ d electrons.

The decrease in the maximum oxidation state after manganese (after iridium and osmium in the second and third series respectively), reflects the difficulty of breaking into a half-filled d orbital. The increasing nuclear charge also helps in binding the d electrons more strongly and thus the highest oxidation state decreases to $+1$ (*e.g.* Cu^+). In fact, for zinc the 3d electrons are not used at all.

However, the highest oxidation is not necessarily the most stable oxidation state.

The stability of higher oxidation state increases with increasing atomic size down the group (as $(n-1)$ d energies become closer to ns energies with increasing atomic size) and the stability of lower oxidation state decreases. Thus, the stability of the $+6$ state for group 6 elements will be

$$W^{6+} > Mo^{6+} > Cr^{6+}$$

(*iii*) Zero and negative oxidation states are also seen in complexes, *e.g.* in carbonyls, $Ni(CO)_4$, $Fe(CO)_5$.

(*iv*) The transition metals usually exhibit their highest oxidation states in compounds with oxygen or fluorine, two of the most electronegative elements.

(*v*) Ti, V, Cr and Mn never form simple ions in their highest oxidation states since this would result in ions of very high charge density. Hence, the compounds in their high oxidation states are either covalently bonded (*e.g.*, TiO_2, V_2O_5, CrO_3, Mn_2O_7) or contain complex ions (*e.g.*, VO_3^-, CrO_4^{2-}, MnO_4^-).

(*vi*) In their lower oxidation states, elements form ionic compounds.

TABLE 11.3 : Oxidation states of transition metals of first series

Oxidation states (Total number of 3d and 4s electrons)	*Sc* 3	*Ti* 4	*V* 5	*Cr* 6	*Mn* 7	*Fe* 8	*Co* 9	*Ni* 10	*Cu* 11	*Zn* 12
+7					7					
+6				6	6	6				
+5			5	5	5		5			
+4		4	4	4	4	4	4	4		
+3	3	3	3	3	3	3	3	3		
+2		2	2	2	2	2	2	2	2	
+1								1		
0			0	0	0	0	0	0		

Important oxidation states are encircled.

Formation of Complexes

Transition metals are known for their ability to form many complex ions. This is attributed to the following factors :

(*i*) Metal ions have vacant d orbitals that can accept one or more electron pairs from molecules or ions (ligands) containing lone pair of electrons. Thus, they show a marked tendency to act as Lewis acids in forming coordination complexes or complex ions

(*ii*) Their high charge density due to the small size and high charge on ions exert the strong electrostatic attraction on the ligands.

(*iii*) Tendency to form several oxidation states.

(*iv*) Not too high basic character. They also form coordination compounds with zero oxidation states, *e.g.*, $Ni(CO)_4$, $Fe(CO)_5$, *etc*. Many such complexes are very stable. Examples are given in Table 11.4.

Formation of Coloured Compounds

A characteristic feature of the transition metal ions is that they are usually coloured. This characteristic distinguishes them from

TABLE 11 : Complex [illegible]

Ligand	*Type of complex*	*Example*	*Name of complex*
Water (H_2O)	*Aqua-*	$[Cr(H_2O)_6]^{3+}$	Hexaaquachromium (III) ion
		$[CrCl_2(H_2O)_4]$	Tetraaquadichlorochromium (III) ion
Ammonia (NH_3)	*Ammine-*	$[Ag(NH_3)_2]^+$	Diamminesilver (I) ion
Hydroxide ion (OH^-)	*Hydroxo-*	$[Zn(OH)_4]^{2-}$	Tetrahydroxozincate (II) ion
Chloride ion (Cl^-)	*Chloro-*	$[CuCl_4]^{2-}$	Tetrachlorocuprate (II) ion
Cyanide ion (CN^-)	*Cyano-*	$[Fe(CN)_6]^{3-}$	Hexacyanoferrate (III) ion
		$[Fe(CN)_6]^{4-}$	Hexacyanoferrate (II) ion
Nitrite ion (NO_2^-)	*Nitro-*	$[Co(NO_2)_6]^{3-}$	Hexanitrocobaltate (III) ion
Carbon monoxide (CO)	*Carbonyl-*	$[Ni(CO)_4]$	Tetracarbonylnickel (0)
Ethane-1,2-diamine (en)	*Ethane-1, 2-diamine-*	$[Cr(en)_3]^{3+}$	Tri(ethane-1, 2-diamine)-chromium (III) ion
edta (or EDTA)	*edta-*	$[Zn(edta)]^{2-}$	edtazincate (II) ion
Cl^-, NH_3	*Mixed*	$[CoCl_2(NH_3)_4]^+$	Tetraamminedichlorocobalt (III) ion
OH^-, H_2O	*Mixed*	$[Fe(OH)_2(H_2O)_4]^+$	Tetraaquadihydroxoiron (III) ion

most compounds of the representative elements. The transition metal ions have unpaired d electrons, which on absorbing visible light (absorb certain wavelengths of light) can jump from one d orbital to another. Thus when certain visible wavelengths are absorbed, the light not absorbed appears to have the complementary colour of the light absorbed. It is this transmitted (unabsorbed) or reflected light (or colour) that appears coloured. The relationship between the colour and wavelength absorbed and the colour observed is given in Table 11.5.

TABLE 11.5 : The relationship between the colour absorbed and the complementary colour observed

Colour absorbed in the visible region	*Complementary colour observed*
Violet	Yellow-green
Indigo	Yellow
Green-blue	Orange
Blue-green	Red
Green	Purple
Yellow-green	Violet
Yellow	Indigo
Orange	Green-blue
Red	Blue-green
Infra-red	White

The Sc^{3+} (aq) ion has no d electrons, and is colourless. In the ions Cu^{+} and Zn^{2+}, with a d^{10} configuration, no d–d transition is possible, and these ions are colourless. Thus, the colour is related to the oxidation state (number of unpaired electrons) of the transition metal ion (Table 11.6). The nature of the complexing ligands affect the energy levels of the d orbitals :

$[Cu(H_2O)_4]^{2+}$	blue
$[Cu(NH_3)_4]^{2+}$	deep blue
$[CuCl_4]^{2-}$	green
$[Cu(CN)_4]^{2-}$	colourless

TABLE 11.6 : Colour of some transition metal ions (aqueous species)

Number of unpaired electrons	*Metal ions*	*Colour observed*
0	Cu^{+}, Zn^{2+}, Sc^{3+}, Ti^{4+}	Colourless
1	Cu^{2+}, V^{4+}, Cr^{5+}	Blue
2	Ni^{2+}, V^{3+}	Green
3	Co^{2+}	Pink
3	Cr^{3+}	Green/violet
4	Fe^{2+}	Green
4	Cr^{2+}	Blue
5	Mn^{2+}	Pale pink
5	Fe^{3+}	Yellow

Magnetic Properties

The ability of magnets to attract iron objects is well known.

Some transition metal compounds also skow magnetic properties. Any species with an unpaired electron is paramagnetic because there is a magnetic moment associated with the spinning electron. The transition metal ions that have unpaired d electrons are paramagnetic. The greater the number of unpaired electrons, the larger the degree of paramagnetism in the compound (Table 11.7).

A paramagnetic substance shows an apparent increase in mass in the applied magnetic field because magnetic attraction augments gravitational attraction. A diamagnetic substance appears to weigh less (Fig. 11.7) as it is repelled out of magnetic field.

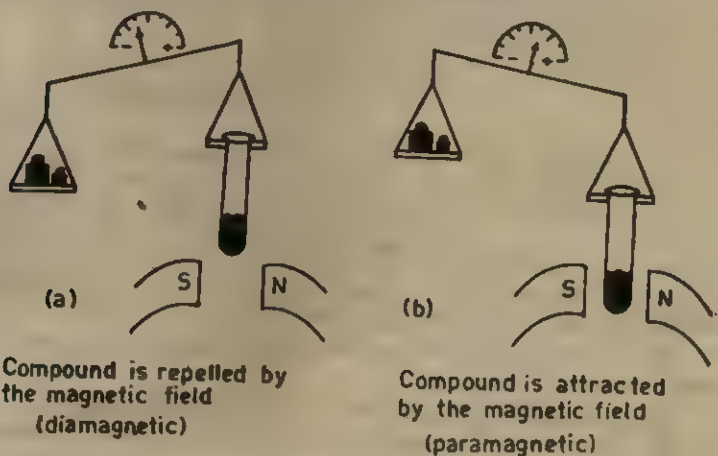


Fig. 11.7. Effect of magnetic field on a diamagnetic and a paramagnetic substances.

Paramagnetism is expressed in terms of Bohr Magneton (BM). When only the spin contribution to magnetic moment is considered,

TABLE 11.7 : Magnetic moments of transitional element ions

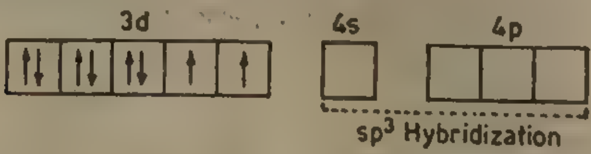
Ion	*Outer electronic configuration*	*Number of unpaired electrons*	*Magnetic moment in Bohr Magnetons* (μ_{BM})	
			Calculated	*Experimental*
Sc^{3+}, K^+, Ti^{4+}, V^{5+}	$3d^0$	0	0·0	0.0 (diamagnetic)
Ti^{3+}, V^{4+}	$-3d^1$	1	1.73	1.73–1.8
Ti^{2+}, V^{3+}	$-3d^2$	2	2.83	2.75–2.90
V^{2+}, Cr^{3+}	$-3d^3$	3	3.87	3.70–3.90
Cr^{2+}, Mn^{3+}	$-3d^4$	4	4.90	4.75–5.0
Mn^{2+}, Fe^{3+}	$-3d^5$	5	5.92	5.7 –6.1
Fe^{2+}, Co^{3+}	$-3d^6$	4	4.90	5.0 –5.7
Co^{2+}, Ni^{3+}	$-3d^7$	3	3.87	4.3 –5.2
Ni^{2+}	$-3d^8$	2	2.83	2.9 –3.4
Cu^{2+}	$-3d^9$	1	1.73	1.7 –2.2
Zn^{2+}, Cu^+	$-3d^{10}$	0	0.0	0.0 (diamagnetic)

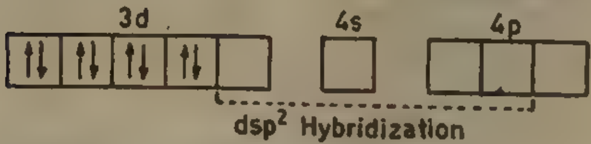
the moment can be related to the number of unpaired electrons, n, by the equation

$$\mu_{BM} = \sqrt{n(n+2)}$$

On the basis of the value of magnetic moment, the structures of compounds can be determined. For example, $K_2[NiCl_4]$ is paramagnetic while $K_2[Ni(CN)_4]$ is diamagnetic.

The electronic configuration of 3d electrons in nickel for paramagnetic $K_2[NiCl_4]$,





Thus, the 4s and 4p orbitals alone are involved in sp^3 hybridization suggesting a tetrahedral structure for $[NiCl_4]^{2-}$.

The electronic configuration of 3d electrons in nickel for diamagnetic $K_2[Ni(CN)_4]$.

Thus, one $3d$, one $4s$ and two $4p$ orbitals could be involved in dsp^2 hybridization suggesting a square planar structure for $[Ni(CN)_4]^{2-}$.

Interstitial Compounds

Transition metals can trap some of the small size atoms like hydrogen, boron, carbon, nitrogen, *etc.*, in their vacant spaces between the crystal lattice forming interstitial compounds—TiC, Mn_4N, Fe_2N, TiH_2. This property differentiates these metals from the elements of other groups. Non-stoichiometric compounds—$Fe_{0.94}O$, $Fe_{0.86}S$, $VH_{0.56}$, $TiH_{1.7}$, *etc.*, are also often classified as interstitial compounds.

Catalytic Activity

Transition metals and their compounds show some catalytic activity. Their activity is attributed to the presence of unfilled or partially filled d orbitals. In some cases these metals provide appropriate surface for reaction and in other cases they form some unstable intermediate complexes (or interstitial compounds), and thus, can provide reaction paths of lower activation energy for normally slow reactions.

Alloy Formation

An alloy is usually composed of two or more metals. Since d-block elements have small and comparable size, they can be mutually substituted by one another in crystal lattices. This type of

substitution results in solid solutions—a class of alloys. For example, chromium dissolves in nickel to form a solid solution in which chromium atoms replace nikel atoms in the crystal lattice of nickel. Interstitial compounds are also quite similar to such solid solutions.

11.3. GENERAL PROPERTIES OF FIRST ROW TRANSITION METAL COMPOUNDS

The transition metals react with various non-metals (oxygen, halogens, sulphur, nitrogen, phosphorus, carbon, *etc.*) to form a wide range of binary compounds. These compounds are found to possess a range of structures, but most commonly network lattices or layer lattices. The bonding in these compounds can for most purposes be regarded as ionic, although many show intermediate character between ionic and covalent.

Oxides

First row transition metals react with oxygen at high temperatures to form oxides of the type, M_2O, MO, M_2O_3, M_3O_4, MO_2, M_2O_5, MO_3 and M_2O_7 with the exception of those (*e g.*, Ag, Au) that are low in the electrochemical series. The important oxides are shown in Table 11.8. Most of them are insoluble in water and either black or coloured. The basic nature of the oxides of the M^{2+} ions increases from Sc to Zn. The oxides of one metal show decreasing basic character, as the oxidation state of the metal increases.

TABLE 11.8 : Oxides of the first row transition elements

	Oxidation States						
Elements	*1*	*2*	*3*	*4*	*5*	*6*	*7*
			Amphoteric line				
Sc			Sc_2O_3				
Ti		TiO	Ti_2O_3	TiO_2			
V		VO	V_2O_3	VO_2	V_2O_5		
Cr		CrO	Cr_2O_3	CrO_2		CrO_3	
Mn		MnO	Mn_2O_3 (Mn_3O_4)	MnO_2			Mn_2O_7
Fe		FeO	Fe_2O_3 (Fe_3O_4)				
Co	Basic oxides	CoO	Co_2O^* (Co_3O_4)	CoO_2	Acidic oxides		
Ni		NiO	Ni_2O_3	NiO_2			
Cu		Cu_2O	CuO				
Zn		ZnO		Ionic or polymerized oxides			Covalent oxides

* Unstable oxides.

Transition metal oxides can be reduced to metals (extraction methods for Fe, Ni, Zn, Mn, *etc*). They react with acids and alkalis to form oxo-ions of transition metals. Metals generally occur in their higher oxidation states combined with oxygen as anions MO_4^{3}

and MO_4^{2-}. The most important of there are the chromate (VI), CrO_4^{2-}; dicromate (VI), $Cr_2O_7^{2-}$; manganate (VI), MnO_4^{2-}; and manganate (VII), MnO_4^-.

In Table 11.8, one can observe the diagonal amphoteric line. The oxides bordering this line have amphoteric character.

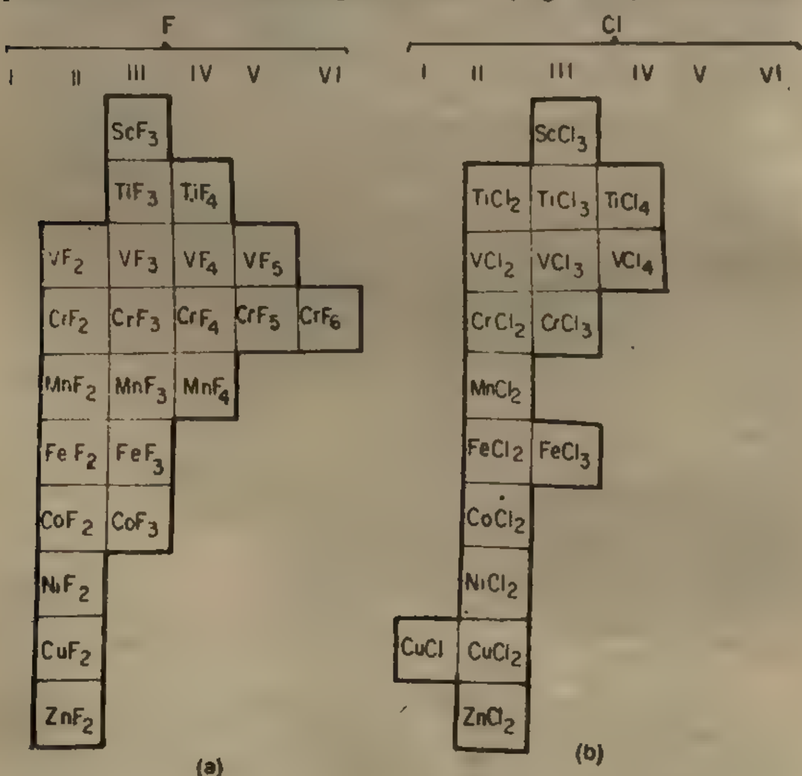
Transition metals also form mixed oxides, non-stiochiometric oxides and spinels. Mixed oxides like Fe_3O_4 ($FeO.Fe_2O_3$) and Mn_3O_4 ($2MnO. MnO_2$) contain the same metal ion in two different oxidation states. In non-stoichiometric oxides, the oxygen-to-metal ratio is found in whole numbers, *e.g.*, $Fe_{0.91}O$, $Fe_{0.95}O$. Defects in crystal lattice (Unit 2) can explain the cause of non-stoichiometry.

A special type of mixed oxide is spinel. $Zn\ Fe_2O_4$ and $Fe(Fe)_2O_4$ are the normal and inverse spinel respectively.

Oxides, of iron, copper, silver, gold, zinc and mercury have already been discussed in Class XI (Unit 15). Some of the oxides are industrially useful.

Halides

The transition elements react with the halogens at high temperatures to form a wide range of halides (Fig. 11.8). The reacti-



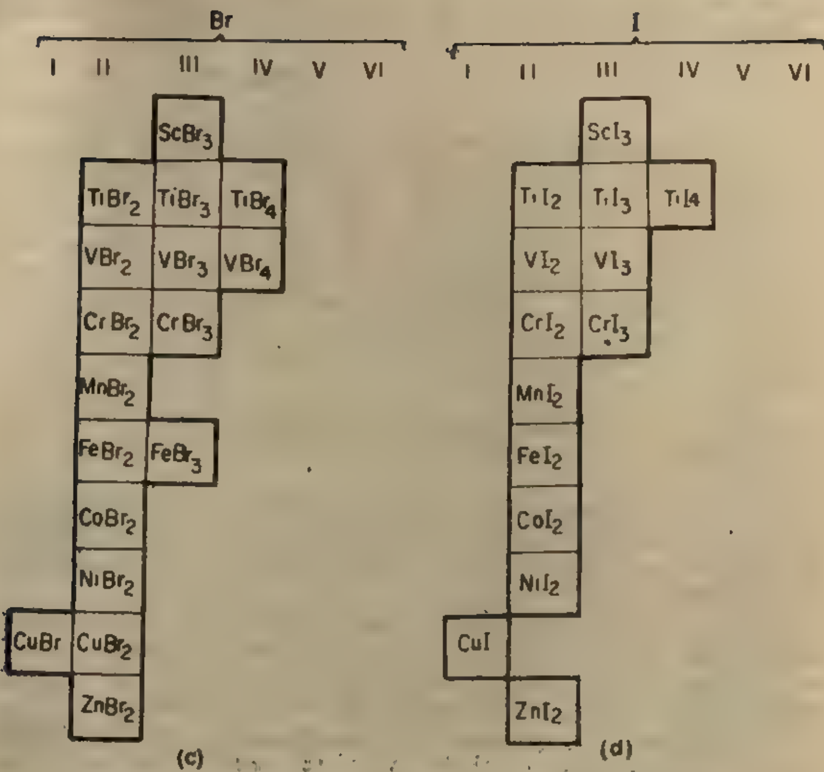


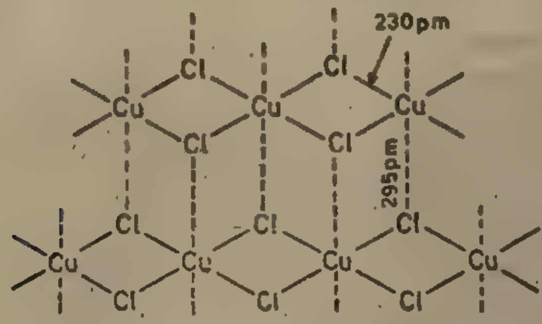
Fig. 11.8. Halides of the first transition metal series (*3* d)

vity of the halogens follows the order : F>Cl>Br>F. Flourine brings out high oxidation states in metals and the fluorides are ionic in character. Metals like. Cr, Mn, Fe, Co, Ni, and Cu form flourides predominantly in their low oxidation states. Difluorides MnF_2, FeF_2, CoF_2 and NiF_2 are ionic solids. Some fluorides, such as MnF_3, CoF_3 and AgF_2 are used as fluorinating agents.

Binary chlorides generally show lower oxidation states of the metals probably due to the larger size of the chlorine compared with the fluorine atom. Lower chlorides are generally ionic although the increased polarizability of chloride ion often results in a different structural type form that of the corresponding fluoride. For example, $FeCl_2$, $CuCl_2$ and $NiCl_2$ possess layer lattices. Chlorides with higher oxidation states of the metals are chiefly covalent as suggested by their volatility and lack of electrical conductivity.

Bromides and iodides show predominantly covalent character. For example, CuF_2 is ionic whilst $CuCl_2$ and $CuBr_2$ are covalent

consisting of infinite chains. The structure of copper (II) chloride is given in Fig. 11.9.



Structure of copper (II) chloride

Fig. 11.9.

Among univalent halides, the silver halides are perhaps the best known examples. Their photosensitive nature is responsible for their extensive use in the photographic process. Copper and gold monohalides are generally not stable.

Dihalides of the transition metals are known in large number. Depending upon the relative size of the cation and anion, they usually assume either the fluorite or rutile structure (Unit 2). Some, which are not hydrolyzed by water, often occur as hydrates.

Trihalides, like the dihalides, are generally inert, and high melting solids. Some of them hydrolyse readily. $FeCl_3$, in the

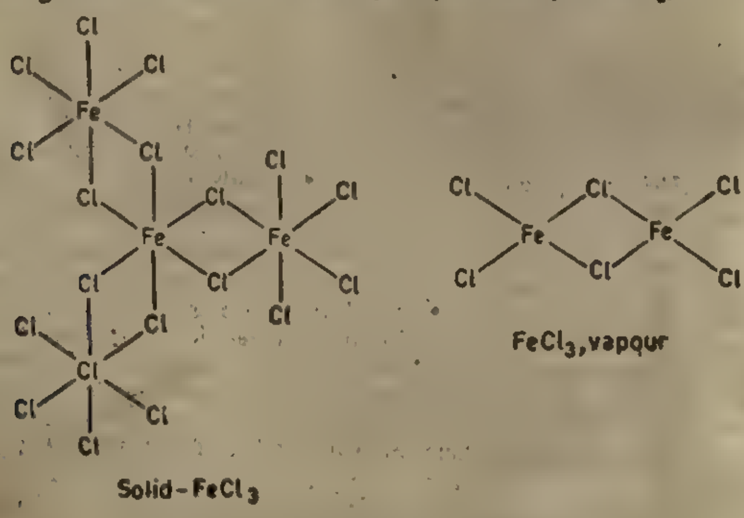


Fig. 10. 11. Structure of ferric chloride

solid state exists in a layer structure in which iron is octahedrally surrounded by six chlorine atoms (Fig 11.10) whereas in the vapour state it exists as dimer, Fe_2Cl_6. Halides of iron, copper, silver, zinc and mercury have been dealt in class XI (Unit 15).

Sulphides

Many transition metals occur in nature as sulphides, *e.g.*, FeS_2, $CuFeS_2$, CuS, MnS, NiS, Ag_2S and HgS. They are usually coloured and macromolecular. They can be obtained as precipitate (insoluble) by the action of H_2S or Na_2S on metal salt solutions. They can also be obtained by heating the metals with sulphur. Sulphur does not bring out the highest oxidation state of the metals. When sulphides or sulphide ores are roasted in air, the metal oxide and sulphur dioxide are formed Oxides can be reduced to yield the metal. Sulphides of Fe, Cu, Ag, Zn and Hg have been dealt in class XI (Unit 15).

11.4. DIFFERENCES BETWEEN THE FIRST AND THE SUBSEQUENT SERIES OF TRANSITION ELEMENTS

The insertation of the lanthanides between barium and hafnium has a bearing effect on the chemistry of the third row transition elements. It upsets the expected regular trend in properties down groups. With the addition of a new shell of electrons between Zr and Hf, an increase in atomic radii and other changes in properties similar to those occurring between Ti and Zr would be expected. This is not evidenced. The f orbitals involved in the third series do not protect the outer electrons well from the increased nuclear charge. As a result, the outer electrons experience the greater effective nuclear charge than expected, and get attracted inward strongly.

This makes the atomic radii of the elements of the third series smaller than expected across the series, and thus, the attraction for electrons becomes greater and the elements have higher electronegativity values. The radii and many other properties of the second and third series are almost identical. The first element differs from the last two (very similar to one another) down the transition series. The effect gradually dies out along the series. (Zn and Cd are more similar in their behaviour than to Hg). Compared to the first series, the elements of the second and third series differ as follows :

1. The elements of the first series are more reactive than those of the other series (have lower reduction potentials).
2. The lower oxidation states become progressively less stable and higher states more stable in going from the first series to the third series (Table 11·9) : Zr (III) is more strongly reducing than Ti (III) ; Mo(VI) is a non-oxidizing state, whereas Cr (VI) is highly oxidizing : Os (VIII) exists, but not Fe (VIII); Cr(II) is known in its compounds but not W(II).

TABLE 11·9 : Formal oxidation states of transition metals

Predominant species	Oxidation state	First row								Second row								Third row							
		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Hf	Ta	W	Re	Os	Ir	Pt	Au
	+8													×								×			
oxides, oxyanions, fluorides	+7				×								×	×							⊕	×			
	+6			×	×	×						⊕	⊕	×	×					⊕	×	×	×	×	
	+5		×	×	×		×				⊕	×	×	×					⊕	×	×	×	×	×	
	+4	⊕	⊕	×	×	×	×	×		⊕	×	×	×	×	×	×		⊕	×	×	×	⊕	⊕	⊕	
	+3	×	×	⊕	×	⊕	×	×	×	×		×	×	⊕	⊕		×	×		×	×	×	×		+
	+2	×	×	×	⊕	×	⊕	⊕	⊕	×	×	×	×	×	×	⊕	×		×	×	×	×		×	×
	+1		×	×	×	×	×	×	×	×	×	×	×	×	×		⊕	×	×	×	×		×		×
	0	×	×	×	×	×	×	×		×		×	×	×	×	×				×	×	×	×	×	
Carbonyls, clusters, organometallics	−1	×	×	×	×		×	×			×		×		×				×		×		×		
	−2			×	×	×						×		×						×					
	−3				×																				

Note ; Circles show most stable oxidation state under common conditions.

3. Elements from the second and third series are less abundant, *e.g.*, technetium is radioactive and not found naturally.
4. Coordination numbers greater than six are rarely encountered with elements in the first series; seven and eight coordination numbers are quite familiar with second and third series, *e.g.*, ZrF_7^{-}.
5. Elements in second and third series have a greater tendency to form polymers. One type of polymer is that containing metal bonds, and this is certainly related to the higher cohesive properties of such elements.

11.5. GENERAL CHEMISTRY OF d-BLOCK ELEMENTS AND GROUP TRENDS

Most of the generalities have already been considered. We will examine a few significant features of the trasition elements in periodic groups.

11.5.1. Group 3 Metals : Scandium Group Metals

Scandium, yttrium, lanthanum and actinium constitute the group 3. Their properties are given in Table 11.10. These elements do not show transitional characteristics as they form compounds only in +3 oxidation state which has the configuration, ns° $(n-1)$ d°. The size and the electropositive nature of the elements increase as the group is descended.

The elements are highly dispersed in the earth's crust, and do not form separate minerals. They are generally obtained by the electrolytic reduction of their trichlorides and trifluorides (Y). The elements are reasonably reactive, second only to the alkali and alkaline earth metals. They react readily with dilute acids (HNO_3) being reduced to NH_4NO_3. Scandium does not react with water, in which it is passivated, while lanthanum decomposes water.

$$2La + 6H_2O \longrightarrow 2La(OH)_3 + 3H_2$$

TABLE 11.10 : Physical properties of group 3 metals

Property	*Sc*	*Y*	*La*	*Ac**
Electronic configuration	[Ar] $3d^1 4s^2$	[Kr] $4d^1 5s^2$	[Xe] $5d^1 6s^2$	[Rn] $6s^1 7s^2$
Metal radius, r/pm	162	181	187	—
Ionic radius (6-coordinate)				
M (III), r/pm	74.5	90.0	103.2	112
Melting point, T/K	1812	1803	1193	1090
Boiling point, T/K	3015	3537	3693	2713
Density at 293 K, ρ/g cm^{-3}	3.0	4.5	6.17	—
Common oxidation state	+3	+3	+3	+3
Electronegativity	1.3	1.2	1.1	1.1

*Radioactive element

11.5.2. Group 4 Metals : Titanium Group Metals

Titanium, zirconium, hafnium and kurchatovium form the titanium group. Titanium is a typical transition element. It is inert at normal temperatures, but above 775K, it reacts vigorously with non-metals to form the compounds $TiCl_4$, TiO_2, *etc.*, and with steam to yield the dioxide and hydrogen. Inspite of its high resistance to corrosion, and high abundance, titanium could not take the place of iron as a structural material. This is due to its high reactivity at high temperatures at which it forms brittle interstitial compounds with carbon and nitrogen. It is extracted from its ores rutile, (TiO_2) and ilmenite ($FeTiO_3$). Industrially, the pure metal is prepared by magnesium reduction of the chloride in an inert atmosphere. Zr and Hf are elements dispersed in earth's crust. Hf is always found with Zr (as zircon, Zr SiO_4)

The atomic and ionic radii increase from Ti to Zr, while the atoms and ions of Zr and Hf, because of lanthanide contraction, are almost equal in size. The properties of *Zr* and Hf are therefore very similar. Some characteristics of the elements are given in Table 11.11. The stable oxidation state of the group is +4 (non-transitional state) though numerous compounds of Ti(III) and a few of Ti(II) are also known. $TiCl_4$ (+4) is largely covalent. Ti in +2 and +3 states forms largely ionic compounds.

Titanium, because of its high thermal stability and corrosion resistance, is an engineering material, and is used in the construction of aircraft, submarines, *etc.* Both Zr and Hf and their alloys are used in nuclear power engineering. TiO_2, and ZrO_2 are used as white pigments. $TiCl_4$ finds use as an important catalyst (Unit 15).

TABLE 11.11 : Physical properties of group 4 metals

Property	*Ti*	*Zr*	*Hf*
Electronic configuration	[Ar] $3d^2 4s^2$	[Kr] $4d^2 5s^2$	[Xe] $4f^{14} 5s^2 6s^2$
Metal radius, *r*/pm	147	160	159
Ionic radius (6-coordinate), M (IV), *r*/pm	60.5	72	71
Melting point, *T*/K	1940	2130	2495
Boiling point, *T*/K	3558	4473	4723
Density at 293 K, ρ/g cm^{-3}	4.50	6.51	13.28
Electronegativity	1.5	1.4	1.3
Common oxidation state	+2, +3, +4	+4	+4

11.5.3. Group 5 Metals : Vanadium Group Metals

This group consists of vanadium, niobium and tantalum. They are obtained from their natural compounds by converting

them first into their oxides, or into simple or complex halides, with subsequent reduction by a metallothermic method.

$$M_2O_5+5CaO \longrightarrow 5Ca+2M$$

Niobium is difficult to separate from tantalum because of the similarities in their properties. Thermal decomposition of their iodides give pure metals. Industrial metals are obtained in the form of ferrovanadium, ferroniobium and ferrotantalum. The steel industry is the main consumer of vanadium.

Vanadium resembles titanium in its physical and chemical properties. The oxidation state +5 is a non-transitional state and is weak oxidizing. At high temperatures, vanadium combines with oxygen forming V_2O_5. Fluorine yields the pentafluoride, VF_5, but chlorine oxidizes the metal to the +4 state, VCl_4. Interstitial compounds are formed with nitrogen, carbon and certain other elements. Vanadium and its oxide (V_2O_5) are used as catalysts.

Niobium alloys are used in jet engines. Tantalum, owing to its high resistance to corrosion, is used in surgical venals and analytical weights.

Alloys based on carbides, nitrides, borides and silicides of Nb and Ta present great interest since they have extraordinary hardness, chemical inertness and heat resistence. Some properties of metals are summarized in Table 11.12.

TABLE 11.12 : Physical properties of group 5 metals

Property	*V*	*Nb*	*Ta*
Electronic configuration	[Ar] $3d^3 4s^2$	[Kr] $4d^4 5s^1$	[Xe] $4f^{14} 5d^3 6s^2$
Metal radius, r/pm	136	148	148
Ionic radius (6-coordinate), M (V), r/pm	54	64	64
Melting point, T/K	2188	2741	3253
Boiling point, T/K	3623	5031	5807
Density at 293 K, ρ/g cm^{-3}	6·11	8·57	16·65
Electronegativity	1·6	1.6	1·5
Common oxidation state	+2, +3, +4, +5	+5	+5

11.5.4. Group 6 Metals : Chromium Group Metals

Chromium, molybdenum and tungsten constitute the group 6 of the periodic table. These high melting metals are very hard. They resist corrosion. They exist in combined states. Chromite ($FeCr_2O_4$) is the most commonly occurring ore of chromium. Generally it is obtained as an alloy (ferrochrome) containing about 60-70% chromium in iron by the reduction of chromite ore $FeCr_2O_4$ ($FeO.Cr_2O_3$) with carbon.

$$FeO \cdot Cr_2O_3+4C \longrightarrow \underbrace{Fe + 2Cr}_{\text{Ferrochrome}} + 4CO$$

Metal is obtained by the reduction of oxide by aluminothermic process.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

The reactions of chromium are similar to those of vandium. It is less electropositive than V. The principal oxidation states are III and VI and there is an unstable divalent state. The highest oxidation state VI is most typical of Mo and W. Coordination numbers of six and four are most typical of Cr, Mo and W. In some compounds, both Mo and W assume 8 coordination number. Group 6 metals predominantly form cation complexes in their lower oxidation states, and anion complexes in higher oxidation states, *e.g.*, $(MoF_8)^{2-}$, $(CrCl_6)^{3-}$, $(Cr(H_2O)_6)^{2+}$, *etc.*

The oxyanious of chromium (VI), CrO_4^{2-} and $Cr_2O_7^{2-}$ (Fig. 11.11) are important species. The two anions are interconvertible.

$$\underset{\text{(Yellow)}}{2\,CrO_4^{2-} + 2H^+} \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} \underset{\text{(Unstable)}}{2HCrO_4^-} \rightleftharpoons \underset{\text{(Orange)}}{Cr_2O_7^{2-}} + H_2O$$

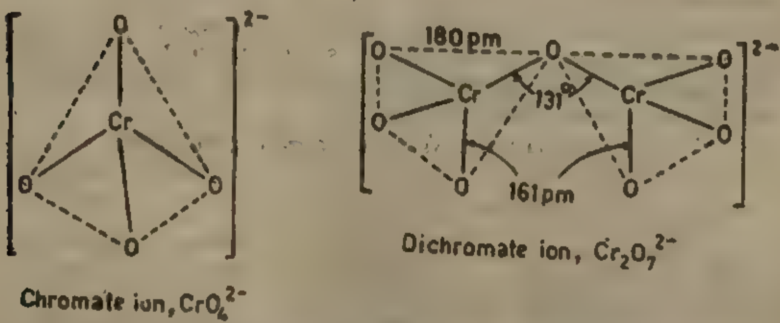


Fig. 11.11. The chromate and dischromate ions.

Some of their physical properties are given in Table 11.13.

Table 11.13 : Physical properties of group 6 metals

Property	*Cr*	*Mo*	*W*
Electronic configuration	[Ar] $3d^5\,4s^1$	[Kr] $4d^5\,5s^1$	[Xe] $4f^{14}\,5d^4\,6s^2$
Metal radius, r/pm	128	139	139
Ionic radius (6-coordinate), M (VI), r/pm	44	59	60
Melting point, T/K	2173	1893	3653
Boiling point, T/K	2963	4923	5773
Density at 293 K, ρ/g cm^{-3}	7.14	10.28	19.3
Electronegativity	1.6	1.8	1.7
Common oxidation state	+3+6 0, +1, +2, +4, +5	+6	+6

All the three metals are used for alloying steel. Chrome steel (Cr FeC) is extremely hard and is used in making safes, armour plates, rails, heavy machinery, *etc.* Stainless steel is a well known alloy (Fe 86%, Cr 13% Ni 1%).

Chromium metal is used extensively in chrome plating. Chromium salts are used (*a*) in tanning leather, (*b*) as mordant in dyeing, (*c*) as oxidizing agents, (*d*) in fire works, (*e*) as refractory materials, (*f*) as catalysts, *etc.*

Both molybdenum and tungsten with carbon, nitrogen, boron and silicon give hard refractory and chemically inert interstitial compounds. Their carbides and nitrides are used in furnace linings and cutting tools, *etc.* Molybdenum is used as a catalyst in the manufacture of ammonia (Haber process). Tungsten wire is used in electric bulb filaments. Its high melting point makes it useful for spark-plug contact points.

Traces of Mo in soil are vital for the normal growth of plant organisms. They probably act as catalyst in the fixation of atmospheric nitrogen.

11.5.5. Group 7 Metals : Manganese Group Metals

Manganese, with the electronic configuration [Ar] $3d^5 4s^2$, is in group 7 of the periodic table. Both technetium (Tc) and rhenium (Re) also belong to this group. Manganese is a hard metal which melts at 1525K. There is a wide range of oxidation states for these metals. Both Tc and Re are quite similar in their chemistry. However, there is a little resemblance to Mn apart from some similarity in the low oxidation states, *e.g.*, in the carbonyls. The +2 oxidation state for manganese is the most stable. The maximum oxidation state of these elements is +7. They resemble their neighbours in their respective periods.

Of all the first row transition metals, Mn shows the greatest range of oxidation states namely −3 to +7. The metal is quite reactive and corrodes in the presence of moisture. The chemistry of its oxides and oxyanions is important. In acid the stable state is Mn^{2+}, while in alkali it is Mn (IV), as the oxide MnO_2. The permanganate ion, MnO_4^- is the most powerful chemical oxidizing agent than can exist in water.

Manganese is the most important element in group 7. Manganese occurs naturally. Its chief ore is pyrolusite, MnO_2. Technetium is radioactive and does not occur naturally. Rhenium is a very rare element. It exists only in trace amounts in certain ores, *e.g.*, molybdenite, MoS_2.

Concentrated (by gravity separation) pyrolusite on heating with Al is violently reduced to metallic manganese. The reaction is much smoother if Mn_3O_4 is used for reduction. Pyrolusite on strong heating gives Mn_3O_4 which can be reduced with carbon or Al. A

pure product is obtained by heating with Al (aluminothermic method)

$$3MnO_2 \longrightarrow Mn_3O_4 + O_2$$

$$Mn_3O_4 + 4C \longrightarrow 3Mn + 4CO$$

$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$$

Presently, manganese is being manufactured by the electrolysis of $MnSO_4$ solution. $MnSO_4$ for the purpose is obtained by treating the roasted ore, Mn_3O_4 with H_2SO_4

$$Mn_3O_4 + 2H_2SO_4 \longrightarrow 2MnSO_4 + MnO_2 + 2H_2O$$

The chief use of manganese is in the production of alloy steels. It imparts hardness and toughness to steal. Ferromanganese alloys (obtained from blast furnace) are employed for making steel. Manganese steel is extremely hard and resistant to wear and abrasion and is used for the jaws of rock crushers, nails, armour plates and heavy machinery. Manganin, an alloy of Cu-Mn-Ni, is used in certain electrical measuring instruments. Manganese works in different ways in alloys of steels. It acts as a scavenger in removing traces of oxygen and sulphur in the steel by forming MnO and MnS. These products are removed as slag in the steel manufacture.

Some of the characteristics of the group 7 metals are summarized in Table 11.14.

TABLE 11.14 : Physical properties of group 7 metals.

Property	*Mn*	*Tc*	*Re*
Electronic configuration	[Ar] $3d^54s^2$	[Kr] $4d^65s^1$	[Xe] $4f^{14}5d^56s^2$
Metal radius, r/pm	127	136	138
Ionic radius (6-coordinate), M (VII), r/pm	46	56	53
Melting point, T/K	1517	2473	3453
Boiling point, T/K	2333	4840	5923
Density at 293 K, ρ/g cm^{-3}	7.43	11.5	21.0
Electronegativity	1.5	1.9	1.9
Common oxidation state	+2, +4, +7, 0, +3, +5, +6	+7	+7

11.5.6. Group 8 Metals : Iron Group Metals

Iron, ruthenium and osmium belong to group 8. Oxidation states +2 and +3 are most characteristic of iron. Iron is the most used of all metals. Its easy extraction and abundance (about 5 per cent of the earth's crust) has made iron indispensable for making everything from automobiles to zither strings. It occurs naturally as haematite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($Fe_2O_3.H_2O$), siderite ($FeCO_3$) and pyrites (FeS_2).

Iron pyrites (fool's gold) is not used for extraction purposes. The reduction of iron ore, known as smelting, is carried out in a blast furnace using CO (from burning of coke in the presence of air). Oxide ore is reduced in stages as the temperature increases.

$$3Fe_2O_3\,(s) + CO\,(g) \xrightarrow{525K} 2Fe_3O_4\,(s) + CO_2\,(g)$$

$$Fe_3O_4\,(s) + CO\,(g) \xrightarrow{675K} 3FeO\,(s) + CO_2\,(g)$$

$$FeO + CO\,(g) \xrightarrow{775K} Fe\,(l) + CO_2\,(g)$$

Iron shows ferromagnetism upto 1040 K. As with previous groups, there is little similarity between the first member and the second and third members of this group. There is some similarity in the chemistry associated with low oxidation states.

General physical properties of the group are listed in Table 11.15.

TABLE 11.15 : Physical properties of group 8 metals

Property	*Fe*	*Ru*	*Os*
Electronic configuration	[Ar] $3d^6 4s^2$	[Kr] $4d^7 5s^1$	[Ke] $5f^{14} 4d^6 6s^2$
Metal radius, r/pm	126	134	136
Ionic radius (6-coordinate), M (IV), r/pm	58·5	62	63
Melting point, T/K	1808	2555 (±20)	3318 (±30)
Boiling point, T/K	3023	4323 (±100)	5298 (±100)
Density at 293 K, ρ/g cm^{-3}	7.87	12 41	22.57
Electronegativity	1.8	2.2	2.2
Common oxidation state	0, +2, +3	+4	+7

Iron has been put to various uses—from using in manufacturing various items to in preparing important and useful alloys. Iron is an essential element of our bodies. It is present in blood as haemoglobin, an oxygen carrier in the body.

Several of its compounds like ferrous sulphate, ferric chloride Mohr's salt find use for a variety of purposes.

11.5.7. Group 9 Metals : Cobalt Group Metals

Cobalt, rhodium and iridium constitute the group 9 of periodic table. Their general characteristics are summarized in Table 11.16. Cobalt is a ferromagnetic metal. Compared with iron, cobalt is a less reactive element. At high temperatures it combines with non-metals such as oxygen and the halogens to produce Co (II) compounds, though with fluorine, CoF_3 is also formed. The most typical oxidation states of cobalt are +2 and +3.

Pure cobalt ores are rarely found. Cobaltite (CoAs S) is a commonly available ore. It is also contained in animal and plant

tissues. The concentrated ore is roasted with silica which forms a slag with impurities. Oxide (Co_3O_4) is reduced with carbon and hydrogen and occasionally by aluminium.

In a number of ways, both Rh and Ir differ from the preceding elements in the second and third transition series. They have a marked resemblance with Co. Their aquous solutions in +3 state contain the hexaaqua ion, just as for Co (III).

Cobalt is used in preparing steels necessary for high speed tools and surgical instruments. Its presence in steel increases toughness and resistance to corrosion. Synthetic Co-60 is used in cancer treatment. Cobalt compounds are used as pigments in glass and porcelain. It is mainly used in electroplating iron and steel articles. A biologically important Co (III) complex is B_{12} (it is a taken as enzyme also).

TABLE 11.16 : Physical properties of group 9 metals

Property	*Co*	*Rh*	*Ir*
Electronic configuration	[Ar] $3d^7\ 4s^2$	[Kr] $4d^8\ 5s^1$	[Xe] $4f^{14}\ 5d^7\ 6s^2$
Metal radius, *r*/pm	125	134	136.5
Ionic radius (6-coordinate), M (IV), *r*/pm	53	60	62.5
Melting point, *T*/K	1768	2233	2716
Boiling point, *T*/K	3373	4033	4823 (±100)
Density at 293 K, ρ/g cm^{-3}	8.90	12.39	22.61
Electronegativity	1.8	2.2	2.2
Common oxidation states	+2, +3	+3, +4, +6	+3, +4, +6

11.5.8. Group 10 Metals : Nickel Group Metals

The chemistry of nickel differs appreciably from that of palladium and platinum (also members of nickel group) Nickel is a ferromagnetic metal. The most characteristic oxidation state of nickel and palladium is +2, and of platinum +4. Compounds of Pt (VI), Pt (II), Pd (IV) are also known. Nickel is quite abundant in the earth's crust ; Pd and Pt are rare elements. There are several ores of nickel, and these usually contain copper also. It is obtained mainly from copper-nickel sulphide ores. The ore is converted into the oxide by roasting and then reduced with carbon.

Most of the nickel is used in alloys (monel, invar, nickel, chrome, *etc.*). It is used in electroplating iron and other metals. Powdered nickel finds application as a catalyst in a variety of reactions, *e.g.*, the hydrogenation of oils and in other organic reactions.

Some of the physical properties of group 10 metals are given in Table 11.17.

TABLE 11.17 : Physical properties of nickel group metals

Property	*Ni*	*Pd*	*Pt*
Electronic configuration	[Ar] $3d^8\ 4s^2$	[Kr] $4d^{10}$	[Xe] $4f^{14}\ 5d^9\ 6s^1$
Metal radius, r/pm	124	137	138.5
Ionic radius (6-coordinate), M (IV), r/pm	48	61.5	62.3
Melting point, T/K	1728	1825	2042
Boiling point, T/K	3193	3213	4443
Density at 293 K, ρ/g cm^{-3}	8.91	11.99	21.41
Electronegativity	1.8	2.2	2.2
Common oxidation state	+2	+2, +4	+2, +4, +6

11.5 9. Metals of Groups 8, 9 and 10

Iron, cobalt and nickel constitute a triad known as **ion triad** because of familiarty in their properties. Similar to ion triad, the platinum metals, *i e.*, ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt) also constitute triads.

1. Iron triad	Fe	Co	Ni
2. Ruthenium triad	Ru	Rh	Pd
3. Osmium triad	Os	Ir	Pt

Triads within themselves bear a strong resemblance, *e.g.*, iron cobalt and nickel exhibit chemical characteristics which are more alike than the characteristics of the elements below them in the periodic table.

As expected, iron, cobalt and nickel fall in line with other elements in the first row of transition metals, *e g.*, in alloys and complex formation. There occurs some differences as well, *e.g.*, Fe, Co and Ni do not form stable oxyanions like CrO_4^{2-} and MnO_4^- and they do not show the same variability in their oxidation states. Similarities and differences are also seen between ruthenium and osmium triads and the elements preceding them in second and third rows of transition elements respectively. As usual, there is a distinct difference between the first element of a vertical group and the others Thus, Fe, Co and Ni are considerably more reactive than the platinum metals. These have been discussed briefly in individual groups.

The platinum metals are very similar to each other both in physical and chemical characteristics and are very inert (dense, very high mp and bp). They recemble silver and gold in many repects. Ru, Rh and Ir are not attacked by mineral acids including aqua regia. Os and Pt dissolve only in aqua regia ; Pd reacts with mineral acids. These elements have the capacity of adsorbing gases. Their chemistry is largely that of complex compounds (a few simple compounds are also known).

The hardness, chemical inertness and resistance to corrosion of platinum metals have led to their use in jewellery (particularly Pd is used), fabrication of laboratory apparatus (crucibles, *etc.*) and in special alloys used for phonograph needles and fountain pen points. Some of them are used as catalysts—platinum is used in the manufacture of both sulphuric and nitric acids ; platinum and palladium for hydrogenation reactions. Metals (particularly Pd) adsorb hydrogen extensively. Palladium is used in coating silver wares to avoid their tranishing because palladium is not affected by H_2S gas.

11.5.10. Group 11 Metals : Copper Group Metals

Copper, silver and gold called coinage metals belong to this group. Their general electronic configuration is $(n-1)d^{10}ns^1$. They have one s electron in their outer orbital but differ from elements of group 1 in that the penultimate shell contains 10 d electrons. They are weak electropositive metals. The metals possess the highest thermal and electrical conductivities. Some of their general characteristics are given in Table 11.18.

TABLE 11.18 : General characteristics of group 11 metals

Property	*Cu*	*Ag*	*Au*
Electronic configuration	$[Ar]3d^{10}4s^1$	$[Kr]4d^{10}5s^1$	$[Xe]5d^{10}6s^1$
Abundance in earth's crust (ppm)	70	0.1	0.005
Atomic radius, *r*/pm	128	144	144
Ionic radius, M^+, *r*/pm	96	126	127
Electronegativity	1.9	1·9	2.4
Ionization energy, *IE* kJ mol^{-1},			
1st	746	731	890
2nd	1959	2123	1973
3rd	3551	3830	2943
Melting point, *T*/K	1356	1233	1336
Boiling point, *T*/K	2868	2483	3243
Density at 293 K, ρ/cm^{-3}	8.95	10.49	19.32
Oxidation state	+1, +2	+1	+1, +3

Silver and gold find use in coins and jewellery. Silver salts are used extensively in photography. The copper, because of its high thermal conductivity is used in manufacturing cooking wares. It also finds use as an electrical conductor. The resistance to corrosion makes copper suitable for water pipes. The coinage metals are used in a variety of alloys (bronze, brass, jeweller's gold, *etc.*) Gold as such or its alloy with copper is used in jewellery. Gold is an article of wealth. Gold has been used in coins and in covering temple domes. Purity of gold is generally given on the carat scale—pure gold is 24 carat.

The detailed chemistry of coinage metals has been discussed in Class XI (Unit 15).

11.5.11. Group 12 Metals : Zinc Group Metals

Zinc, cadmium and mercury constitute group 12. Their characteristic electronic configuration is $(n-1)d^{10}ns^2$. The d shell being complete, the metals show few properties which are associated with the transition metals. These metals resemble copper, silver and gold in having completely filled d orbitals in the penultimate shell but are comparatively more active In their compounds +2 oxidation state is very common which is formed by losing ns^2 electrons. The existence of +1 oxidation state has been well characterized in the case of mercury but it does not exist with either zinc or cadmium. Despite the stability of inner d^{10} core, complexes with 4-coordinate and 6-coordinate numbers are very common.

Unlike transition metals, zinc and cadmium have much in common (occur together in nature and their chemistry is almost identical). These metals are better reducing agents (Unit 5) than coinage metals inspite of the fact that they have much higher ionization potentials.

The reactivity decreases as we move from zinc to cadmium to mercury. Some general properties of the metals are summarized in Table 11.19 on the next page.

Zinc, cadmium and mercury are used extensively in dry cell batteries. Zinc is used to galvanize iron for protecting the latter from rusting. Alloys of zinc are used widely.

Cadmium's chief use is in plating iron. Its deposit is smooth and has self heating property after it is scratched.

Mercury is used in a variety of electrical devices (*e.g.*, switches mercury vapour lamp), thermometers, barometers). It is also used in alloys, called amalgams. Dental amalgam contains merury, silver, tin and copper.

TABLE 11·19 : General properties of group 12 metals

Property	*Zn*	*Cd*	*Hg*
Electronic configuration	$[Ar]3d^{10}4s^2$	$[Kr]4d^{10}5s^1$	$[Xe]5d^{10}6s^2$
Abundance in earth's crust (ppm)	132	0.15	0.08
Atomic radius, r/pm	135	151	154
Ionic radius, M^{2+} r/pm	74	95	102
Electronegativity	1.6	1.7	1.9
Ionization energy, IE/kJ mol^{-1}			
1st	906	876	1007
2nd	1733	1631	1810
Melting point, T/K	693	594	235
Boiling point, T/K	1180	1040	630
Density at 298 K, ρ/g cm^{-3}	7.1	8.7	13.6
Common oxidation state	+2	+2	+1, +2

Organomercury compounds are used as fungicides and as timber preservatives. Sodium and zinc amalgams (alloys of mercury with sodium and zinc) are used as reducing agents.

The detailed chemistry of zinc and mercury has been discussed in Class XI (Unit 15).

11.6. SOME IMPORTANT COMPOUNDS

Potassium Dichromate $K_2Cr_2(VI)O_7$

Important oxo-compounds of Cr(VI) are formed by oxidation of Cr(III) salts with sodium peroxide, or, on a large scale, by heating chromite ore ($FeCr_2O_4$) with Na_2CO_3 in the presence of air.

$$\underset{(4FeCr_2O_4)}{4FeO.Cr_2O_3(s)}+8Na_2CO_3(s)+7O_2(g)\longrightarrow 8Na_2CrO_4(s)+2Fe_2O_3+8CO_2(g)$$

The soluble Na_2CrO_4 is dissolved in weter and separated from Fe_2O_3. Yellow chromate solution on acidifying produces sodium dichromate.

$$2Na_2CrO_4+H_2SO_4\longrightarrow \underset{(Orange)}{Na_2Cr_2O_7}+Na_2SO_4+H_2O$$

Sodium dichromate solution, thus obtained, is treated with potassium chloride to get less soluble orange crystals of potassium dichromate.

$$N_2Cr_2O_7 + 2HCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Potassium dichromate is an orange-red crystalline substance (m.p. 671K). An aqueous solution of dichromate on treating with alkali turns yellow due to the formation of CrO_4^{2-} ions which on acidifying gives again $Cr_2O_7^{2-}$ ions.

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

The two ions, CrO_4^{2-} and $Cr_2O_7^{2-}$ (Fig. 11.11), are inter-convertible by treatment with acid or alkali.

$$\underset{\substack{\text{Chromate ion} \\ \text{(Yellow)}}}{2CrO_4^{2-} + 2H^+} \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} \underset{\text{Unstable}}{2HCrO_4} \rightleftharpoons \underset{\substack{\text{Dichromate} \\ \text{(Orange)}}}{Cr_2O_7^{2-} + H_2O}$$

In concentrated acid, the oxide Cr(VI)O_3 is produced.

$$K_2Cr_2O_7 + H_2SO_4 \rightleftharpoons 2CrO_3(s) + Na_2SO_4(aq) + H_2O(l)$$

The oxide is the anhydride of the acid, H_2CrO_4, which cannot be isolated since the conjugate base dimerizes

$$2HCrO_4^-(aq) \rightleftharpoons Cr_2O_7^{2-} + H_2O(l)$$

The mixture of CrO_3 and conc. H_2SO_4, termed chromic acid, is a good cleaning agent for glass wares because of its oxidizing ability.

Both chromate and dichromate ions are oxidants. The dichromate ion acts as a powerful oxidant in acidic solution. It can act as oxidant in netural solution also. Acidified $K_2Cr_2O_7$ will oxidize iodides to iodine, ferrous salts to ferric, sulphites to sulphates, sulphides to sulphur, stannous salts to stannic, sulphur dioxide to sulphuric acid, *etc.*

$$6I^- \longrightarrow 3I_2 + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad E^0 = 1{\cdot}33 \text{ V}$$

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

Similarly, the oxidation of other reducing agents will be effected by $Cr_2O_7^{2-}$ ions.

$$Fe^{2-} \longrightarrow Fe^{3+} + e^-$$

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$H_2S \longrightarrow S + 2H^+ + 2e^-$$

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$

By adding these half reactions for the reducing agents to the half reaction for $Cr_2O_7^{2-}$ the complete ionic equation is obtained.

Dischromate ions also oxidize certain organic compounds, such as alcohols to aldehydes and then to acids (Unit 7 and 8).

In basic solution (where the CrO_4^{2-} ion exists) the oxidizing power is greatly reduced.

$$CrO_4^{2-}+4H_2O+3e^- \longrightarrow Cr(OH)_3(s)+5OH^- \qquad E^0=-0{\cdot}13\ V$$

The oxidizing action of dichromate ion has been used in estimating some reducing agents. Thus, $K_2Cr_2O_7$ find application as a primary standard in volumetric analysis. Some insoluble chromates, notably Ag_2CrO_4 (brick red) $BaCrO_4$ and $PbCrO_4$ (yellow) are made use of in analytical work. It is used in chrome tanning, electroplating, dyeing, calicoprinting, photography, *etc.* Potassium dichromate is also used for the preparation of chromium compounds like chrome alum, K_2SO_4, $Cr_2(SO_4)_3.24H_2O$; chrome yellow, $PbCrO_4$; chrome red, $PbCrO_4$; PbO ; *etc.* It is widely used as an oxidizing agent in organic chemistry.

Chromyl chloride test

The oxidation of halide ions is very slow. $K_2Cr_2O_7$ on heating with concentrated sulphuric acid and a chloride salt produces orange-red vapour of chromyl chloride, CrO_2Cl_2.

$$K_2Cr_2O_7+4NaCl+6H_2SO_4 \longrightarrow 2KHSO_4+4NaHSO_4+3H_2O +2CrO_2Cl_2$$

This reaction is the basis of chromyl chloride test used for the detection of Cl^- ions. In the detection of Cl^- ions, chromyl chloride vapours are passed through alkali and CrO_4^{2-} ions are produced. These ions with acetic acid and lead acetate give yellow precipitate of lead chromate, $PbCrO_4$.

$$CrO_2Cl_2+2NaOH \longrightarrow Na_2CrO_4+2HCl$$

$$Na_2CrO_4+Pb(OOCCH_3)_2 \longrightarrow \underset{\text{(Yellow ppt.)}}{PbCrO_4}+2NaOOCCH_3$$

Potassium Permanganate, KMn(VII)O_4

Potassium permanganate is one of the best known compounds of manganese It is manufactured by fusing concentrated pyrolusite with potassium hydroxide in a stream of air (sometimes a little amount of KNO_3 or $KClO_3$ is also added). The green melt of potassium manganate so formed is cooled and leached with a little water.

$$MnO_2+4OH^-+O_2 \xrightarrow{\text{Heat}} MnO_4^{2-}+O_2+2H_2O$$

Green crystals of K_2MnO_4 are obtained on evaporation under vacuum.

$KMnO_4$ is produced either by electrolytic oxidation or by oxidation with ozone (or chlorine or carbon dioxide) of a basic solution of K_2MnO_4.

Electrolytic oxidation

$$\underset{\text{(Basic green solution)}}{MnO_4^{2-}} \longrightarrow \underset{\text{(Purple)}}{MnO_4^-} + e^- \text{ (Anode reaction)}$$

Oxidation by chlorine or ozone

$$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^- + 2OH^- + O_2$$
$$2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^- + 2Cl^-$$

On concentrating or evaporating the solution, purple coloured crystals of $KMnO_4$ are deposited.

On a small scale (or in a laboratory) MnO_4^- ions can be produced by the oxidation of Mn^{2+} ions with sodium bismuthate or PbO_2 (or $S_2O_8^{2-}$) in the presence of excess of nitric acid. This reaction is carried out at a moderate temperature.

$$2Mn^{2+} + 5BiO_3^- + 16H^+ \longrightarrow 2HMnO_4 + 5Bi^{3+} + 7H_2O$$

The latter reaction is employed for the detection of manganese in qualitative analysis. The reaction with $S_2O_8^{2-}$ is used in quantitative analysis of manganese.

Potassium permanganate is a deep purple solid (bears a metallic luster) which dissolves in water to give a characteristic red violet solution. It decomposes slowly on exposure to light depositing MnO_2, the reaction being catalyzed by light. Acidic solution is also unstable and decomposes slowly (catalyzed by sunlight).

$$4MnO_4^- (aq) + 4H^+ (aq) \longrightarrow 4MnO_2 (s) + 3O_2 (g) + 4OH^- (aq)$$

Hence solution of $KMnO_4$ is generally stored in coloured bottles. On strong heating it decomposes.

$$2KMnO_4 \xrightarrow{\text{(Strong heating)}} K_2MnO_4 + MnO_2 + O_2.$$

and in a stream of hydrogen it yields KOH and manganous oxide.

$$2KMnO_4 + 5H_2 \longrightarrow 2KOH + 2MnO + 4H_2O$$

Permanganate is a strong oxidizing agent under both acidic and alkaline conditions. In acidic medium

$$MnO_4^- (aq) + 8H^+ (aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O \text{ (l)}$$

In alkaline medium

$$MnO_4^- (aq) + 2H_2O \text{ (l)} + 3e^- \longrightarrow MnO_2 (s) + 4OH^- (aq)$$

It also acts as an oxidizing agent in neutral medium.

$$MnO_4^- (aq) + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

In alkaline or neutral solution, MnO_4^- acts as a weak oxidizing agent

In acidic medium, potassium permanganate oxidizes ferrous to ferric, oxalate to carbon dioxide, nitrite to nitrate, iodide to iodine, halogen acids to halogens, *etc*. Some of these reactions may be represented as :

$$2MnO_4^- + 16H^+ + 10Fe^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 10Fe^{3+}$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \xrightarrow[\text{(Hot)}]{} 2Mn^{2+} + 8H_2O + 10CO_2$$

$$2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

Similarly it can oxidize sulphides to sulphur, sulphur dioxide to sulphuric acid, sulphites to sulphates, arsenites to arsenates, hydrogen peroxide to oxygen, *etc*. Hydrochloric acid is not used for making $KMnO_4$ solution acidic since it is oxidized to chlorine.

$$2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

If insufficient acid is added the reduction of MnO_4^- only goes as for as MnO_2.

Alkaline permanganate oxidizes iodides to iodates, ethylene to glycol, *etc*.

$$I^- + 2MnO_4^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-$$

$$3\begin{array}{c}CH_2\\ \| \\ CH_2\end{array} + 2MnO_4^- + 4H_2O \longrightarrow 3\begin{array}{c}CH_2OH\\ | \\ CH_2OH\end{array} + 2MnO_2 + 2OH^-$$

Treatment of permanganate with conc. H_2SO_4 gives the explosive green oil Mn_2O_7. Treatment with conc. alkali gives the green manganate ion,

$$2MnO_4^- + 2OH^- \longrightarrow MnO_4^{2-} + \tfrac{1}{2}O_2 + H_2O$$

Addition of acid to manganate, or allowing the aqueous solution of MnO_4^{2-} to stand, results in a disproportionation reaction given by the equation.

$$3Mn\,(VI) \longrightarrow 2Mn\,(VII) + Mn\,(IV)$$

i.e. $$3MnO_4^{2-} + 4H_2O \longrightarrow 2MnO_4^- + MnO_2 + 4OH^-$$

Manganese in MnO_4^- undergoes sp^3 hybridization, and thus, four oxygen atoms are arranged tetrahedrally (Fig. 11.12) around manganese.

$KMnO_4$ is widely used in redox volumetric estimation of ferrous salts, oxalates *etc*., and in qualitative analysis, for the detection of halides, oxalates, sulphites, *etc*. Alkaline permanganate (Baeyer's reagent) is widely used in the preparation of saccharin, vitamin C and nicotinic acid. It is used in disinfecting water both for drinking and industrial purposes.

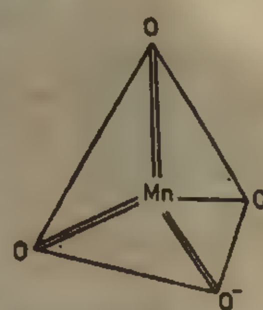


Fig. 11.12. Structure of permanganate ion, MnO_4^-

Compounds of Iron

The sulphates of iron are generally employed for studying the chemistry of iron. Iron (II) is readily available as $FeSO_4.7H_2O$ and as double salt $FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr's salt) and iron (III) as $Fe_2(SO_4)_3.nH_2O$ and the alum $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$. Some of these sulphates have already been discussed in Class XI (Unit 15).

Among the halides only $FeCl_3$ and $FeBr_3$ are known. Ferric iodide does not exist because ferric ions are reduced by I^- in aqueous solution. The chemistry of $FeCl_3$ has already been discussed in Class XI (Unit 15).

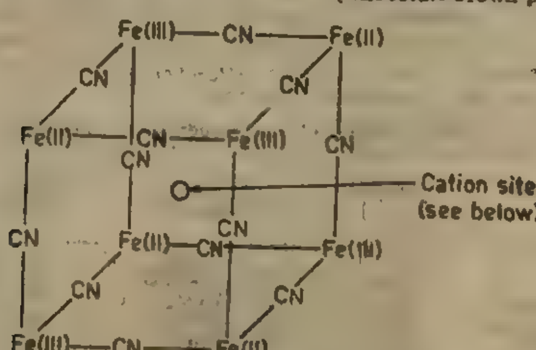
The cyanide complexes of Fe (II) and Fe (III), $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ are stable in water solution. If either of the two cyanides is treated with an aqueous solution of iron in the other oxidation state, a deep blue compound called prussian blue or turn bull's blue is produced.

$$[Fe(CN)_6]^{4-} + 3Fe^{3+} \longrightarrow \text{Prussian blue}$$
$$[Fe(CN)_6]^{3-} + Fe^{2+} \longrightarrow \text{Turnbull's blue}$$

Both these compounds are the same compound. They can be formulated as K[Fe (II) Fe (III) $(CN)_6$] and has a simple cubic structure (Fig. 11.13).

Cyanide complexes are useful in qualitative analysis of Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+} ions *etc.* Potassium ferrocyanide reacts with Cu^{2+} ions forming coloured precipitate.

$$2Cu^{2+}(aq) + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN)_6]$$
(Chocolate brown ppt.)



[Fe(III) Fe(III)$(CN)_6$]	No K^+ ions; all iron atoms Fe(III)
K[Fe(II) Fe(III)$(CN)_6$]	K^+ ions in half the cubes
K_2[Fe(II) Fe(II)$(CN)_6$]	K^+ ions in the centre of all cubes; all iron atoms Fe(II)

Fig. 11.13. Structure of [Fe (II) Fe (III) $(CN)_6$]$^-$ and related compounds.

Compounds of Copper and Silver

Divalent copper is well known in a wide variety of blue octahédral complexes of $Cu(H_2O)_4.SO_4.H_2O$, $[Cu(NH_3)_4]SO_4.H_2O$ and $Cu(NO_3)_2.3H_2O$.

The chemistry of copper sulphate has already been discussed in Class XI (Unit 15).

Silver nitrate, known as lunar caustic, is one of the most important soluble salts of silver. We have already discussed this compound in Class XI (Unit 15).

11.7. INNER TRANSITION METALS

The two series of inner transition metals that follow lanthanum (Z=57) and actinium (Z=89) are often referred to as the lanthanides (or lanthanons) and the actinides respectively. They are also collectively called f-block elements as the underlying 4 f or 5 f orbitals $(n-2)$ are progressively filled. The filling of 4 f and 5 f orbitals gives rise to a series of 14 elements each.

11·7·1. Lanthanides

The elements (Z, 58 to 71) which follow lanthanum (Z=57) are called lanthanides or lanthanons. They have no counterparts in the previous periods of the periodic table. The main feature of their chemistry is their great similarity to one another, and this caused difficulties f separation at one time, since they are always found in nature together. The similarity in properties is illustrated strikingly by the values of the reduction potentials. Important properties of lanthanides are given in Tables 11.20-11.21. Several of the lanthanides are used as catalysts, in producing coloured glasses, in welder's and glass blower's goggles, in synthetic gems and in phosphors in colour television screens.

TABLE 11·20 : General atomic properties of lanthanides

Lanthanide	*Symbol*	*Electronic Configuration*	*Atomic number*	*Relative atomic mass*
Cerium	Ce	$[Xe]\ 4f^1 5d^1 6s^2$	58	140.12
Praseodymiun	Pr	$[Xe]\ 4f^3 6s^2$	59	140.91
Neodymium	Nd	$[Xe]\ 4f^4 6s^2$	60	144.24
Promethium	Pm	$[Xe]\ 4f^5 6s^2$	61	—
Samarium	Sm	$[Xe]\ 4f^6 6s^2$	62	150.36
Europium	Eu	$[Xe]\ 4f^7 6s^2$	63	151.96
Gadolinium	Gd	$[Xe]\ 4f^7\ 5d^1\ 6s^2$	64	157.25
Terbium	Tb	$[Xe]\ 4f^9\ 6s^2$	65	158.93
Dysprosium	Dy	$[Xe]\ 4f^{10}\ 6s^2$	66	162.50
Holmium	Ho	$[Xe]\ 4f^{11}\ 6s^2$	67	164.93
Erbium	Er	$[Xe]\ 4f^{12}\ 6s^2$	68	167.26
Thulium	Tm	$[Xe]\ 4f^{13}\ 6s^2$	69	168.93
Ytterbium	Yb	$[Xe]\ 4f^{14}\ 6s^2$	70	173.07
Lutetium	Lu	$[Xe]\ 4f^{14}\ 5d^1\ 6s^2$	71	174.94

TABLE 11·21 : General physical properties of lanthanides

Lanthanide	Metal radius, r/pm	Ionic radius, M (III), r/pm	Melting point T/K	Boiling point, T/K	Density at 298 K, ρ/g cm^{-3}	Sum of first three ionization energies. IE/kJ mol^{-1}	Electrode potential at 298 K, E°/V $M^{3+}(aq)+3e^- \rightarrow M(s)$	Oxidation [redacted]
Ce	181.8	102	1077	3743	6.77	3515	−2.48	+3, +4
Pr	182.4	99	1208	3293	6.48	3623	−2.46	+3, +4
Nd	181.4	98.3	1297	3300	7.00	3705	−2.43	+3
Pm	183.4	97	—	—	7.2	—	−2.42	+3
Sm	180.4	95.8	1345	2037	7.54	3898	−2.41	+2, +3
Eu	208.4	94.7	1099	1712	5.25	4033	−2.41	+2, +3
Gd	180.4	93.8	1585	3273	7.89	3744	−2.40	+3
Tb	177.0	92.3	1629	3073	8.25	3792	−2.39	+3, +4
Dy	178.1	91.2	1680	2873	8.56	3898	−2.35	+3, +4
Ho	176.2	90.1	1734	2873	8.78	3937	−2.32	+3
Er	176.1	89.0	1770	3173	9.05	3908	−2.30	+3
Tm	175.9	88.0	1818	2000	9.32	4038	−2.28	+2, +3
Yb	193.3	86.8	1097	1700	6.97	4197	−2.27	+2, +3
Lu	173.8	86.1	1925	3600	9.84	3898	−2.27	+3

Electronic configuration. Chemical properties of the elements are governed largely by the electrons in the outermost shell. The electronic configuration (Table 11.21) of a lanthanide is

$$[Xe]\,4f^{n+1}5d^{0}6s^{2} \quad \text{or} \quad [Xe]\,4f^{n}\,5d^{1}\,6s^{2}$$

In the filling of the f orbital there is some indication of particular stability at f^0, f^7, and f^{14} configurations. Since the f orbitals are buried deep within the atom, these electrons are not involved in the bonding, and hence, have a minor impact on the properties of the elements.

Oxidation states. Ionization energy values of lanthanides are low (sum of first three ionization energies are given in Table 11·21). The compounds formed by these elements are ionic and M^{3+} state dominates the chemistry of these elements. The M^{2+} and M^{4+} ions are also formed particularly when the metals attain an f^0 (Ce^{4+}), f^7 (Eu^{2+}, Gd^{3+}, Tb^{4+}) and f^{14} (Yb^{2+}, Lu^{3+}) configurations corresponding to an empty, half-filled and completely full f levels.

They have a poor tendency to form coordination compounds.

Colour. Most trivalent lanthanide ions are coloured both in aqueous solution and in the solid states and a correlation between the number of f-electrons present and colour has been found. The ions with n more electrons than La^{3+} often have a same colour to those with a $(14-n)$ f electrons (Table 11.22).

TABLE 11·22 : Colour of trivalent lanthanide ions

Ion	*Number of 4f electrons*	*Colour*	*Ion*	*Number of 4f eletrons*	*Colour*
La^{3+}	0	Colourless	Lu^{3+}	14	Colourless
Ce^{3+}	1	Colourless	Yb^{3+}	13	Colourless
Pr^{3+}	2	Green	Tm^{3+}	12	Green
Nd^{3+}	3	Lilac	Er^{3+}	11	Lilac
Pm^{3+}	4	Pink	Ho^{3+}	10	Pale yellow
Sm^{3+}	5	Yellow	Dy^{3+}	9	Yellow
Eu^{3+}	6	Pale pink	Tb^{3+}	8	Pale pink
Gd^{3+}	7	Colourless	Gd^{3+}	7	Colourless

Thus, lanthanide ions having no unpaired electrons (*e.g.* La^{3+}—$4f^0$; Lu^{3+}—$4f^{14}$; Yb^{2+}—$4f^{14}$) or half-filled (f^7) configuration (*e.g.*, Gd^{3+}, Eu^{2+}) are colourless. Lanthanide ions with 2 to 6 unpaired electrons are coloured. Hence coloure is presumably due to the presence of unpaired electrons.

Magnetic properties. The f^0 and f^{14} states (as in La^{3+}, Ce^{4+} and Lu^{3+}) have no unpaired electrons. These are, therefore, diamagnetic. All other f states that contain unpaired electrons are coloured and are paramagnetic.

The magnetic susceptibilities of the trivalent ions do not obey the spin only formula because of the contribution made to the

magnetic moment by the orbital moments of the 4f electrons. Fig. 11·14 shows the variation in magnetic moments of the ions M^{3+} for lanthanides.

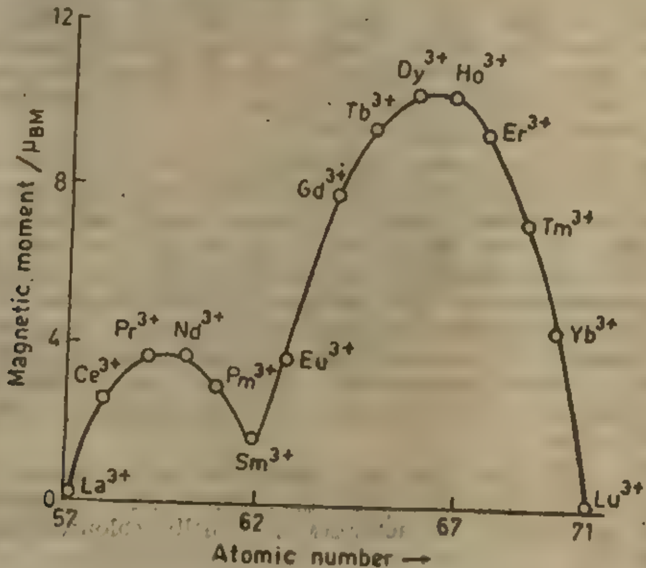


Fig. 11.14. Magnetic moments of the lanthanide ions, M^{3+}

Atomic and ionic radii. The metal radii of the lanthanides and their ionic radii (tripositive) (Table 11·21) steadily decrease from Ce to Lu with increasing effective nuelear charge as the 4f shell is successively filled. This is because the mutual shielding of 4f electrons from nuclear charge is poor. Thus successive addition of 4f electrons increases the effective nuclear charge without a comparable increase in the screening effect. As a consequence, the whole 4f electron shell contracts on passing across the lanthanides. This steady decrease in metallic and ionic radii across the lanthanides is known as the **lanthanide contraction.**

As a result of lanthaide contraction, unexpectly the atomic sizes and chemistry of the third row transition series (5d series) closely resemble those of the second row transition elements (4d series). The normal size increase from Sc to Y to La disappears after the lanthanides. Thus, the pairs of elements such as Zr-Hf, Nb-Ta, Mo-W have nearly identical sizes. They have similar chemical properties and their separation is very difficult. This is a direct consequence o, lanthanide contraction. The effect is also responsible for the chemical similarity within the lanthanides themselves. A general decrease in ionic radii across the series results in corresponding increase in the polarizing power of the ions and in the stability of the complex ions.

11.7.2. Actinides

The elements beyond actinium (Z=89), from thorium (Z=90) to lawrencium (Z=103) consitute the actinides series. In this series of elements the 5f orbitals are progressively filled. The name 'actinide' is derived from actinium. The elements are collectively called actinides or actinons. Most of the members of the actinide series are known as the result of synthesis and do not occur in nature. They are all radioactive. Some of their properties are summarized in Tables 11.23−11.24.

The general electronic configuration of actinides is $[Rn]5f^{0-14}$ $6d^{0-2}$ $7s^2$ (Table 11.23). The actinides like the lanthanides, also form compounds in oxidation state +3. Several higher oxidation states are possible for each of the earlier member of the series (Table 11.24). This is attributed to the fact that 5f, 6d and 7s levels are of comparable energies. Thus thorium (IV), protoactinium (V) and uranium (VI), compounds are more stable than the compounds of these elements in +3 oxidation state. Americium onwards, oxidation state +3 becomes progressively more important as the atomic number increases and the chemistry of these elements is similnr to that of lanthanides.

The similarities with the lanthanides are attributed to the presence of partially-filled shells of electrons. The compounds of both the lanthanides and actinides are usually coloured and paramagnetic.

TABLE 11.23 : General atomic properties of actinides

Actinide	*Symbol*	*Electronic configuration*	*Atomic number*	*Relative atomic mass*
Thorim	Th	$[Rn]\,6d^2 7s^2$	90	232.038
Protoactinium	Pa	$[Rn]\,5f^2\,6d^1\,7s^2$	91	231.036
Uranium	U	$[Rn]\,5f^3\,6d^1\,7s^2$	92	238.029
Neptunium	Np	$[Rn]\,5f^4\,6d^1\,7s^2$	93	237.048
Plutonium	Pu	$[Rn]\,5d^6\,7s^2$	94	239.052
Americium	Am	$[Rn]\,5f^7\,7s^2$	95	241.057
Curium	Cm	$[Rn]\,5f^7\,6d^1\,7s^2$	96	244.063
Berkelium	Bk	$[Rn]\,5f^9\,7s^2$ or $5f^8\,6d^1\,7s^2$	97	249.075
Californium	Cf	$[Rn]\,5f^{10}\,7s^2$	98	252.082
Einsteinium	Es	$[Rn]\,5f^{11}\,7s^2$	99	253.085
Fermium	Fm	$[Rn]\,5f^{12}\,7s^2$	100	257.095
Mendelevium	Md	$[Rn]\,5f^{13}\,7s^2$	101	256.094
Nobelium	No	$[Rn]\,5f^{14}\,7s^2$	102	255.093
Lawrencium	Lr	$[Rn]\,5f^{14}\,6s^1\,7s^2$	103	256.099

TABLE 11·24 : General physical properties of actinides

Actinide	Metal radius, r/pm	Ionic radius, M (III) r/pm	Melting point, T/K	Boiling point, T/K	Density 298 K, ρ/g cm^{-3}	Oxidation states*
Th	179	—	2023	5123	11.78	3, 4
Pa	163	104	1825	4500	15.37	3, 5
U	156	102.5	1403	4203	19.05	3, 4, 5, 6
Np	155	101	913	5508	20.45	3, 4, 5, 6, 7
Pu	159	100	913	3503	19.86	3, 4, 5, 6, 7
Am	173	97.5	1443	2873	13.67	2, 3, 4, 5, 6
Cm	174	79	1613	—	13.51	3, 4
Bk	170	96	1259	—	14.78	3, 4
Cf	186 ± 2	95	1173	—	—	2, 3
Es	186 ± 2	—	1133	—	—	2, 3
Fm	—	—	—	—	—	2, 3
Md	—	—	—	—	—	2, 3
No	—	—	—	—	—	2, 3
Lr	—	—	—	—	—	2, 3

*The most important oxidation states are encircled.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

11·1. Choose the correct answer of the four alternatives given for the following questions :

(i) Which of the following elements does not belong to the first transition series ?

(a) Ag (b) Fe
(c) Cr (d) Ti.

(ii) Which of the following is not a characteristic property of transition elements ?

(a) Variable oxidation states
(b) Formation of coloured compounds
(c) Formation of interstitial compounds
(d) Natural radioactivity.

(iii) Which the following ions is expected to have the highest magnetic moment ?

(a) Cu^{2+} (b) Mn^{2+}
(c) Ti^{2+} (d) Zn^{2+}.

(iv) The yellow colour of chromates changes to orange on acidification due to the formation of

(a) CrO_3 (b) CrO_4^{2-}
(c) $Cr_2O_7^{2-}$ (d) $Cr_3O_{10}^{2-}$.

(*v*) The outer electronic configuration of chromium is

(*a*) $3d^4\,4s^2$ (*b*) $3d^6\,4s^0$

(*c*) $3d^6\,4s^1$ (*d*) $3d^5\,4s^1$.

(*vi*) The principal oxidation state of lanthanides is

(*a*) +2 (*b*) +3

(*c*) +4 (*d*) +6.

(*vii*) Which of the following statements is not correct ?

(*a*) The oxides and hydroxides of d-block elements are less basic than than those of the f-block elements.

(*b*) The sizes of the atoms and ions of d-block elements are relatively smaller than those of the f-block elements.

(*c*) The tendency of d-block elements to form complexes is less than that of f-block elsments ?

(*d*) Both lanthanides and actinides constitute the f-block elements.

(*viii*) The lanthanide contraction relates to

(*a*) atomic radii (*b*) densities

(*c*) valence electrons (*d*) oxidation states.

(*ix*) The most strongly oxidizing state of manganese known in aqueous solution is

(*a*) +7 (*b*) +2

(*c*) +3 (*d*) +4.

(*x*) Which of the following electronic configurations will have the highest magnetic moment.

(*a*) d^6 (*b*) d^4

(*c*) d^7 (*d*) d^5.

11.2. Fill in the blanks with appropriate words.

(*i*) The lower oxidation states often act as............agents and form.......

(*ii*) The higher oxidation states serve as............agents and form.........

(*iii*) Oxyanious are common in the case of............oxidation states.

(*iv*) Most transition metals ions have............electrons and are............

(*v*) The gradual............in size across a series of transition metals is accompanied by a gradual............in ionization energy.

(*vi*) The two series of inner transition elements result from the filling of the............orbitals.

(*vii*) The colour of the transition metal ions is related to the............of the element and also to the nature of the............

(*viii*) The hydrated Fe (III) has ....electrons.

(*ix*) The............contribute to the catalytic activity of many transition elements and their compounds.

(*x*) In transition metal compounds,..............are responsible for the colours of the transition metal compounds.

11.3. Choose the correct statements of the following and write true (T) or false (F).

(*i*) The first, second and third row transition metals have closely similar chemistry.

(*ii*) Transition metals display a wide range of oxidation states.

(*iii*) Metal ions with the same d electron configuration have a number of similar chemical properties.

(*iv*) The transition metal halides and oxides in low oxidation states have covalent structures.

(*v*) The oxyanions of chromium (*vii*), CrO_4^{2-} and $Cr_2O_7^{2-}$ are inter-convertible.

(*vi*) Chromate salts are more soluble than dichromate salts.

(*vii*) Treatment of MnO_4^- iron with conc. H_2SO_4 gives MnO_2.

(*viii*) The anhydrous halides of ion have ionic structures in the solid state.

(*ix*) Both cobalt and nickel are ferromagnetic in nature.

(*x*) Fifteen elements constitute the lanthanide series of elements.

Short Answer Questions

11.4. (*i*) How does the ionic-covalent character of the compounds of a transition metal vary with its oxidation state ?

(*ii*) Why does a transition series contain 10 elements.

(*iii*) Why do transition elements show similarities along the horizontal period ?

(*iv*) The second ionization energies of both Cr and Cu are higher than those of the next element. Explain.

(*v*) How do you account for paramagnetism and colours observed for compounds of transition metals.

TERMINAL QUESTIONS

11.1. Define transition elements. How are they distinguished from other elements ?

11.2. What are the general properties of the d-block elements ?

11.3. (*i*) Why are most transition metal compounds coloured ?

(*ii*) Elements with atomic numbers 23, 24 and 25 have 3, 6 and 5 unpaired electrons. Explain the irregularity in the number of unpaired electrons.

(*iii*) Compare the electronic configurations of calcium and zinc, both as atoms and as ions with +2 state.

(*iv*) Why are the elements with atomic numbers from 57-71 placed at one place ?

(*v*) Why are complex ions readily formed when H_2O molecules react with cations but not when hydronium ions (H_3O^+) react ?

11.4. Explain the following observations made in the chemistry of chromium and manganese :

1. Chromium (+2) compounds are good reducing agents.
2. Chromium (+2) compounds are better reducing agents than Mn (+2) compounds.
3. Chromium is much less corroded in air than iron.
4. Chromium shows anomalous electronic configuration.
5. The reaction of $KMnO_4$ with conc. H_2SO_4 is explosive.
6. Potassium permanganate solution is not kept in the sunlight.
7. All the compounds of chromium and manganese are not of the same colour.
8. Standard solutions of both $KMnO_4$ and $K_2Cr_2O_7$ are not prepared in dilute sulphuric acid.

11.5. Why do the transition elements exhibit variable oxidation states, form coloured compounds, undergo complexation and exhibit paramagnetic behaviour?

11.6. How is the magnetic moment related to the number of unpaired electrons for first transition series? Calculate the magnetic moments for Ti^{4+}, V^{4+}, V^{3+}, Cr^{3+} and Fe^{3+} ions.

11.7. (*a*) Discuss the nature of transition metal complexes, in particular the nature of the metal, the donor atoms and the type of bonding.

(*b*) Write the formulae for the following ions:

(*i*) Cyanide complex, (*ii*) Ammonia complex, (*iii*) Halide complex, and (*iv*) Hydrated complex.

11.8. Discuss the origin of (*a*) colour, and (*b*) paramagnetism in transition metal complexes.

11.9. (*a*) Both d-block and p-block elements show variation in oxidation states. Point out the differences with reasons for these variations.

(*b*) In what ways are the chromium group elements different from other transition metals?

(*c*) In alkaline solution dichromate ions are converted into chromate ions and in acidic solution reverse happens. Explain.

11.10. Comment on the following:

(*a*) Almost all the transitional elements utilize d orbitals in forming compounds but zinc, cadmium and mercury do not utilize.

(*b*) Zinc is more reactive than magnesium.

(*c*) Copper (+2) forms stable compounds but CuI_2 is not obtained.

(*d*) Among transition elements the first element in a group normally differs from other elements but in zinc group both zinc and cadmium are very closely related.

11.11. (*a*) What are transition elements? Name the elements of d-block which are not considered as transition elements?

(*b*) Point out the difference between the electronic configurations of transition elements and representative elements.

11.12. Starting from chromite and pyrolusite how could one prepare $K_2Cr_2O_7$ and $KMnO_4$ respectively.

11.13. Name four important elements in the first transition series. Why are they chiefly metallic in character? Mention two elements which are amphoteric and support your reply with reactions.

11.14. Mention some of the important uses of chromium, manganese, iron and cooper.

11.15. Give preparation, properties and uses of the following:

(*i*) Silver nitrate, (*ii*) Potassium permanganate, (*iii*) Copper sulphate, and (*iv*) Mohr's salt.

11.16. Discuss the following tests with chemical equations:

(*a*) Chromyl chloride test, (*b*) Ring test for nitrate, (*c*) Silver nitrate test for thiosulphate ion, and (*d*)] Detection of manganese using sodium bismuthate.

11.17. (*a*) Write equations representing the oxidation of MnO_4^{2-} on (*a*) acid solution, (*b*) alkaline solution, and (*c*) neutral conditions.

(*b*) Discuss the formation of MnO_4^{2-} species and its stabilization.

(*c*) Why is MnO_2 so stable?

(*d*) Is it possible to use HCl instead of H_2SO_4 when MnO_4^- is used as an oxidizing agent in acid conditions?

11.18. Discuss the formation of Prussian blue. What is the origin of the intense blue colour ?

11.19. What are inner transition elements ? How do they differ from transition elements ?

11.20. What is meant by 'lanthanide contraction' ? What are its consequences ?

11.21. Discuss the oxidation states, colour and magnetic properties of lanthanides and actinides.

11.12. What are actinides ? Name two naturally occurring actinides. Discuss the general characteristics of actinides.

11.23. Describe the importance of transition elements in biological systems.

11.24. Why do inner transition metals show much less variation in properties than the transition metals ?

11.25. Why are trends in variations of properties of successive d-transition elements less regular than trends among successive representative elements ?

ANSWERS TO SELF ASSESSMENT QUESTIONS

11.1. (*i*) (*a*), (*ii*) (*d*), (*iii*) (*b*), (*iv*) (*c*), (*v*) (*d*) (*vi*) (*b*), (*vii*) (*c*), (*viii*) (*a*), (*ix*) (*a*), (*x*) (*d*).

11.2. (*i*) reducing, hydroxides, (*ii*) oxidizing, acids, (*iii*) higher, (*iv*) unpaired, para magnetic (*v*) decrease, increase (*vi*) 4f and 5f (*vii*) oxidation state, complexing liquid (*viii*) five unpaired, (*ix*) empty low energy d orbitals, (*x*) transition of an electron between d orbitals.

11.3. (*i*) F, (*ii*) T, (*iii*) T, (*iv*) F, (*v*) T, (*vi*) F, (*vii*) F, (*viii*) T, (*ix*) T, (*x*) F.

11.4. (i) With increasing oxidation state, more valence shell electrons get involved in bonding, the atomic core become less shielded, and the electronegativity of the atom increases. Thus, the ionic character of the bonds, in the sense $A^{\delta+}—B^{\delta-}$ decreases with increasing oxidation state.

(ii) There are five d orbitals in an energy level and each orbital contains 2 electrons. As we move from one element to the next, an electron is added and therefore complete filling of these five *d* orbitals with electrons requires 10 electrons.

(iii) This is because the electronic configuration remains the same in the outermost shell, of all the transition elements.

No doubt, the 4s level being energetically more stable than the 3d level is preferred over 3d. However, once the 3d level, which of course is closer to the nucleus is occupied by electrons, these repel the 4s electrons even further from the nucleus to a higher energy level. Now when metals form ions, they lose electrons from the 4s level before the 3d level. This means that all transition metals the have similar chemical properties.

(iv) This is because the outer electronic configuration of Cr^+ 4s $3d^5$ (half filled) and that of Cu^+ is $3d^0$ (completely filled). Thus the second ionization of Cr means the removal of one electron from the highly stable $3d^5$ core. Similarly, the second ionization of copper involves the removal of one electron from the highly stable $3d^{10}$ core.

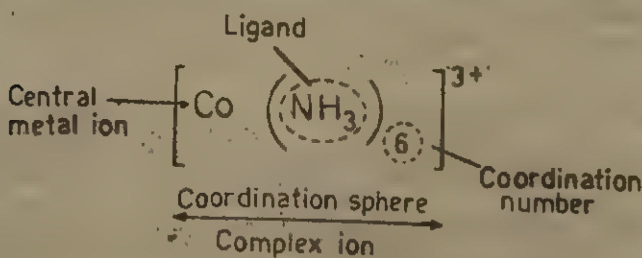
(v) Both the colour and paramagnetism are related to the presence of unpaired *d* electrons. The transition of an electron between d orbitals of different energies are responsible for the colours of most transtion metal compounds.

The greater the number of unpaired electrons, the larger the degree of paramagnetism in the compound.

UNIT 12

Coordination Compounds and Organometallics

An interesting characteristic of transition metals is their ability to form complexes, such as $[(Co(NH_3)_6]^{3+}$. Complex ions are composed of a central metal ion surrounded by a cluster of anions or molecules called ligands. Non-bonded pairs of electrons on the ligand form co-ordinate bonds to the centra' ion by donating these unshared electron pairs into vacant orbitals of the transition metal ion.



UNIT PREVIEW

12.1. Introduction.
12.2. Coordination compounds.
12.3. Nomenclature of coordination compounds.
12.4. Isomerism in coordination compounds.
12.5. Bonding in coordination compounds.
12.6. Stability of coordination compounds in solution.
12.7. Importance of coordination compounds.
12.8. Organometallic compounds.
Self assessment questionc Terminal questions Answers to self assessment questions.

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Define coordination and organometallic compounds and state the factors responsible for their formation.
2. Describe the structural features of coordination complexes : ligands, geometry, magnetic properties, and colour.
3. State the salient features of Werner's coordination theory.
4. Describe a few methods of their preparation ; and general properties.

5. Name the coordination compounds according to IUPAC and write their formulae from their names.
6. Identify the types of structural isomerism possible in coordination compounds.
7. Recognize the structural features of coordination compounds that lead to the possibility of stereoismers.
8. Describe the bonding in complexes in terms of the valence bond theory, correlating hybridization and geometry.
9. State the merits and demerits of valence bond theory.
10. Give the cause of colour and magnetic properties in complexes on the basis of crystal field theory.
11. Comment on the stability and application of coordination compounds.
12. Classify the organo metalliccompounds on the basis of bonding.
13. Comment on the nature of bonding involved in the organometallic compounds.
14. Give a few methods for the preparation of organometallic compounds and their applications.

12.1. INTRODUCTION

Prehaps the area of chemistry most widely developed in the last four decades has been that of coordination chemistry, applied particularly to complexes of transition metals. One of the characteristic properties of the transition elements is their ability to form complex ions. **Coordination compounds** or, as they are generally called, **complexes** are playing increasingly important roles in industry, ranging from anticorrosion agents and soil treatment agents to medicinal agents, which certainly testify for their importance in contemporary life. Many biolsogically important substances, such as chlorophyll, haemoglobin and vitamin B_{12} are coordination compounds in which large, complicated organic species are bound to a metal ion. Haemoglobin, a protein in blood, contains iron bound to a large organic group (porphyrin). It is the carrier of oxygen in blood. Vitamin B_{12} (cyano cobalamin) that occurs in animals and micro-organisms is a cobalt (III) complex. It is needed for normal blood formation and that it is necessary for the synthesis of DNA. Chlorophyll, a naturally occurring magnesium (II) complex, plays an important role in plant metabolism. A variety of metallurgical processes, industrial catalysts and analytical reagents make use of coordination compounds. Many complex minerals which consist of metal oxides and sulphides are solid-state coordination compounds. In this Unit, we shall study some features the chemistry of coordination compounds. Along with coordination compounds, we shall also study some aspects of the chemistry of organometallic compounds which contain metal-carbon bonds.

12.2. COORDINATION COMPOUNDS

As early as 1798, it was discovered by Tassaert that an ammoniacal solution of a cobalt (II) salt on exposure to air, assumes brown colour. Later, it was established by Fremy that the brown coloured salt of cobalt is the oxidized cobalt (III) compound com-

combined with ammonia having a formula $CoCl_3.6NH_3$. The complexity of these cobalt compounds, along with that of the solid hydrates of transition metal compounds and other complex compounds ($NiCl_2.6NH_3$, $CuSO_4.4NH_3.H_2O$, $CoCl_3.5NH_3$, $PtCl_2.2NH_3$, *etc.*) posed a major problem for chemists in the 19th century. Their structures and bonding could not be explained on the basis of the existing theories of bonding. The simple valence rule could not explain the apparent anomaly of the reaction of a 'valence satisfied' compound such as $CoCl_3$ with a 'valence satisfied' molecule such as NH_3 to give the compound $CoCl_3.6NH_3$. However, the bonding involved in their formation could only be explained by Alfred Werner in 1891 at the age of 25. In recognition of his pioneering work on coordination compounds, Werner was awarded Nobel Prize in Chemistry in 1913.

Prior to Werner's rationalisation, the coordination compounds were regarded as addition compounds and their formulae of were written with dots, $CrCl_3.6H_2O$, $AgCl.2NH_3$, *etc.* just like double salts such as Mohr's salt $FeSO_4.(NH_4)_2SO_4, 6H_2O$. The double salt solution dissociates into its components (*i.e.*, Fe^{2+}, NH_4^+, SO_4^{2-}) and its properties are expected for solutions made by mixing the individual salts. However, a solution of $AgCl.2NH_3$ or $[Ag(NH_3)_2]Cl$ behaves entirely differently from either a solution of (insoluble) AgCl or a solution of NH_3.

All cations in solution form some sort of complex aggregates, for example, H_3O^+ and Na^+ (aq), but these are usually non-stoichiometric complexes resulting from ion-dipole attractions. Discrete stoichiometric complex ions are observed for transition metals in their higher oxidation states. Such complexes also dissociate in solution. The variation in composition that is possible is illustrated by some Pt (IV) complexes with NH_3 and Cl^- (Table 12·1).

TABLE 12·1. Varying composition of Pt (IV) complexes with Cl^- and NH_3

Complex	*Number of ions per compound*	*Number of Cl^- ions per compound*	*Nature of complex part*
$K_2[PtCl_6]$	3	0	Anion
$K[PtCl_5(NH_3)]$	2	0	Anion
$[PtCl_4(NH_3)_2]$	0	0	Electrically neutral
$[PtCl_3(NH_3)_3]Cl$	2	1	Cation
$[PtCl_2(NH_3)_4]Cl_2$	3	2	Cation
$[PtCl(NH_3)_5]Cl_3$	4	3	Cation
$[Pt(NH_3)_6]Cl_4$	5	4	Cation

Thus, within these compounds, there exist two types of bonding, as is clear from Table 12·1 :

(*i*) predominantly covalent bonding which unites the atoms in the coordination spheres and (*ii*) predominantly electrovalent bonding which units the oppositely charged ions. There are complexes in which all the bonding is predominantly covalent, *e.g.*, $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_2Cl_4]$ in which platinum is in the +2 and +4 respectively.

The formation of a complex is the result of a Lewis acid-base type of interaction, in which one atom with vacant orbital (generally the metal) attracts the electron pairs donated by Lewis bases or **ligands** (from the Latin, ligandus, 'binding'). The ligands together with the central atom constitute the **coordination sphere**. The total number of the ligands bound around a metal ion is called the **coordination number** of the metal ion.

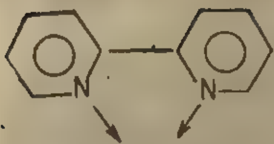
The charge remaining on the central atom or ion when the ligands are removed together with their lone pairs is the **oxidation number** of the metal in the complex. Coordination complexes in which the metal ion has an oxidation state greater than +3 are not common. Metals in oxidation states greater than +3 are significantly electronegative that they show strong oxidizing ability. As a result, they remove electrons from the ligands and become reduced.

Ligands can be of several types, viz., nonodentate (from the Latin dentatus, 'having teeth') bidentate, tridentate......polydentate (many teeth) depending on the number of coordinating atoms present in them.

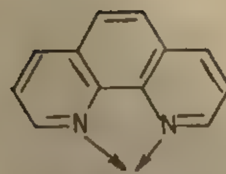
Mono- or unidentate ligands. They have only one donor atom, *i.e.*, they can only form one bond to a central atom or ion. It may be an anion such as F^- Cl^-, Br^-, I^-, NO_2^-, CN^-, SO_4^{2-} or a neutral molecule such as NH_3, RNH_2, H_2O, CH_3CN, PPh_3, Py.

However, there are ligands possessing more than one donor atom and these are able to 'bite' the central atom in more than one coordination position. These are termed polydentate or **chelate ligands** as the bonds formed by them are thought to resemble the claws of a crab (Greek : chele) and such compounds are named as **chelate compounds** or **chelates**. An example of such a ligand is ethylenediamine (en), $\ddot{N}H_2CH_2CH_2\ddot{N}H_2$ in which the lone pairs on the two nitrogen atoms are capable of simultaneous coordination. It is thus a **bidentate** ligand.

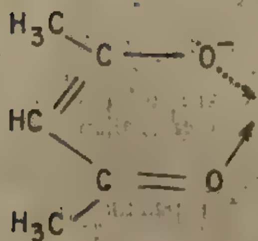
Bidentate ligands. They have two donor atoms. Some more examples of bidentate chelate ligands are :



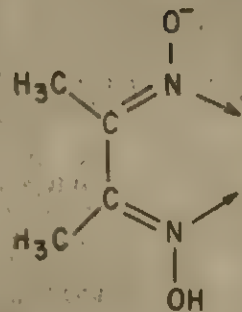
2,2′-Dipyridine (dipy)



1,10-Phenanthroline (phen)

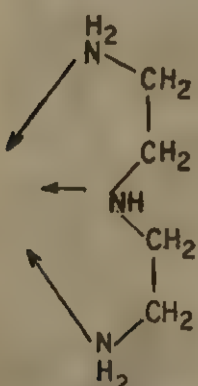


Oxalato

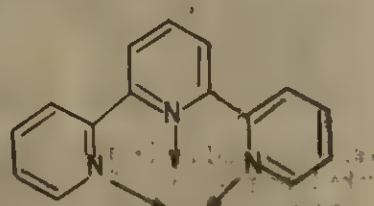


Dimethylglyoximato

Tridentate ligands. They have three coordinating centres. Some examples of tridentate chelate ligands are :

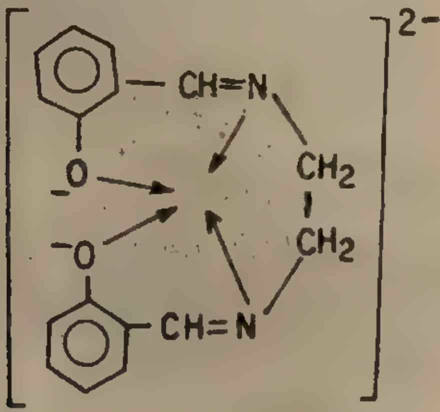


Diethylenetriamine (dien)

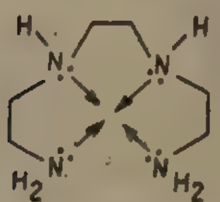


2, 2′, 2″ Terpyridine (terpy)

Tetradentate ligands. They have four coordinating centres. Examples

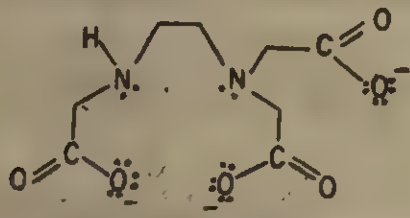


Ethylenebis (salicylaldimine) ion.



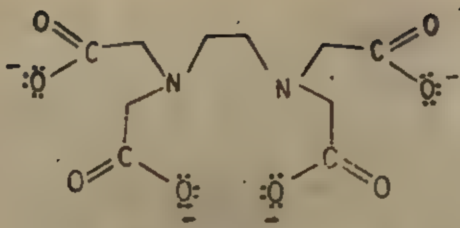
Triethylenetetramine (trien)

Pentadentate ligands. They have five coordinating centres. Example



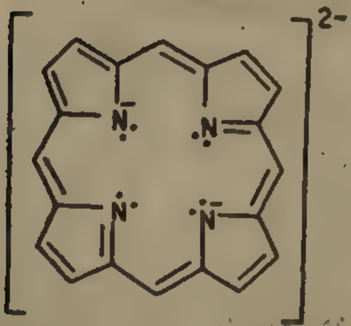
Ethylenediaminetriacetato

Hexadentate ligands. They coordinate to a metal ion at six places. Example

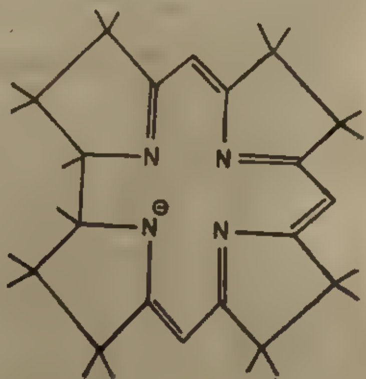


Ethylenediaminetetraacetate
($EDTA^{4-}$)

Another important type is macrocyclic ligand. These are closed system and have normally four or more coordination sites (donor atoms). The donor atoms are most commonly nitrogen atoms, though oxygen or sulphur atoms, or a mixed set also occur. Two simple examples are :



Porphyrin



Corrin

12·2·1. Werner's Coordination Theory

The essential features of 'Werners' coordination theory are listed below :

Every elements exhibit two different Winds of valencies, *viz* ,

(*a*) primary valence (ionizable) depends on the charge on the cation and is satisfied by the equal but opposite charge of the anions. For example

$$Cu^{2+}, 2Cl^- \text{ or } Co^{3+}, 3Cl^-$$

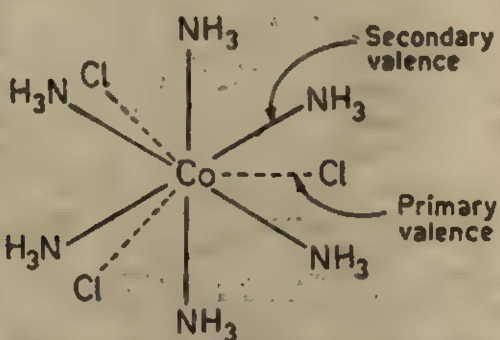
Its attachment to the metal is shown by dotted lines. The primary valence is called the oxidation state of the metal (modern terminology).

(*b*) secondary valence (non-ionizable) is a directed covalent valence. It is satisfied by either neutral molecule or negative ions.

Each metal has a characteristic secondary valence, which is independent of the primary valence.

For example, Co (III) has 6 secondary valence. This is now called the coordination number of a central metal, and it varies with the size and charge of the cation. Its attachment to the metal is shown by thick lines.

Accordingly the complex, $CoCl_3.6NH_3$ may be portrayed as :



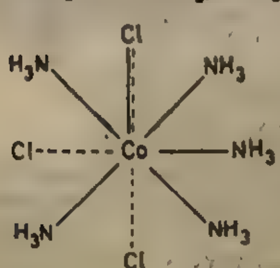
As, it has already been pointed out that the coordination number of cabalt is always 6, the secondary valence (non-ionizable) in the other coordination compounds given below must be 6 because of ammonia and cov alently bonded chloride ions. For example,

$CoCl_3.5NH_3$—one Cl^- ion satisfies both the primary and secondary valencies,

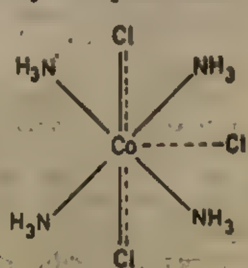
$ClCl_3,4NH_3$—Two Cl^- ions satisfy both the primary and secondary valencies.

$COCl_3.3NH_3$—Three Cl^- ions satisfy both the primary and secondary valencies.

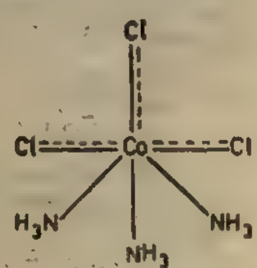
Now, the three complexes of cobalt, $CoCl_3 . 5NH_3$, $COCl_3$ $4NH_3$ and $CoCl_3,3NH_3$ may be represented as :



$CoCl_3 \cdot 5NH_3$



$CoCl_3 \cdot 4NH_3$



$CoCl_3 \cdot 3NH_3$

(Cl^- ions attached both by dotte as well as thick lines meet the requirement of both the primary and secondary valencies)

Now on the basis of the precipitation of Cl^- ions by adding $AgNO_3$, the cobalt (III) compounds can be formulated as given in Table 12·2.

Table 12·2. Ammonia complexes of cobalt (III)

Compound	*Colour*	*Number of Cl^- ion precipitated*	*Modern formulation*
$CoCl_3 . 6NH_3$	Orange yellow	3	$[Co(NH_3)_6] Cl_3$
$CoCl_3 . 5NH_3 . H_2O$	Rose	3	$[Co(NH_3)_5H_2O] Cl_3$
$CoCl_3 . 5NH_3$	Purple	2	$[[Co(NH_3)_5 Cl]Cl_2$
$CoCl_3 . 4NH_3$	Green	1	$[Co(NH_3)_4 Cl_2] Cl$
$CoCl_3 . 3NH_3$	Blue-green	0	$[[Co(NH_3)_3 Cl_3]$

The conductivity measurement of the various coordination compounds also provided enough support to the Werner's model. Further the ligand statisfying the secondary valence always adopt fixed positions in space giving a definite geometry.

12·2·2. Preparation of Coordination Compounds

Here we classify and discuss some of the most important methods.

(*i*) Substitution reactions

These are of two main types depending on the reaction conditions ; either with or without solvents. For example, the addition of aqueous (aq) ammonia to an aqueous solution of $NiCl_2$ forms the hexaamminenickel (II) ion :

$$\underset{\text{(Green)}}{[Ni(H_2O)_6]^{2+}(aq)}+6NH_3(aq) \longrightarrow \underset{\text{(Blue)}}{[Ni(NH_3)_6]^{2+}(aq)}+6H_2O(l)$$

Similarly, blue coloured tetraammine copper (II), $[Cu(NH_3)_4]^{2+}$ is formed from $CuSO_4.5H_2O$ and ammonia. Ferrous sulphate and excess of KCN solution give potassium hexacyanoferrate (II) $K_4[Fe(CN)_6]$

$$\underset{\text{(Light blue)}}{[Cu(H_2O)_4]^{2+}}(aq)+4NH_3(aq) \rightarrow \underset{\text{(Deep blue)}}{[Cu(NH_3)_4]^{2+}}+4H_2O(l)$$

$$[Fe(H_2O)]_6^{2+}(aq)+6CN^-(aq) \rightarrow [Fe(CN)_6]^{4-}+6H_2O(l)$$

If the ligand being added is an anion, neutral or anionic complexes are obtained. Chromium (III) reacts with acetylacetonate ion ($acac^-$) to form a neutral complex :

$$[Cr(H_2O)_6]^{3+}(aq)+3CH_3-\underset{\underset{\displaystyle O}{|}}{C}=CH-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3(aq)$$

$$\longrightarrow Cr(acac)_3(aq)+6H_2O(l)$$

(*ii*) **Direction reaction**

It involves the reaction between a Lewis acid and a Lewis base in the absence of water. An inertsolvent or a gaseous phase can also be used.

On mixing VCl_4 and pyridine in toluene at 250 K, $VCl_4 . 2py$ is precipitated.

$$VCl_4 + 2py \xrightarrow[250\ K]{Toluene} VCl_4 . 2py$$

The reaction of carbon monoxide with nickel metal is used in the industrial purification of nickel metal. This does not require any solvent. Impure nickel is made to react with carbon monoxide at 335 K to form gaseous $Ni(CO)_4$:

$$Ni\ (s) + 4CO(g) \xrightarrow{335\ K} \underset{\text{(Colourless)}}{Ni\ (CO)_4\ (g)}$$

The impurities associated with nickel do not react and are left behind.

(*iii*) **Redox reactions**

The preparation of many complexes involves either oxidation or reduction. Co (II) is more readily available than Co (III), and Co (II) complexes are easily obtained. To synthesize a CO (III) complex of ethylenediamine (en), first Co (II) complex is prepared which, in turn, is oxidized

$$[Co(H_2O)_6]^{2+} . (aq) + 3\ en\ (aq) \longrightarrow [Co\ (en)_3]^{2+}\ (aq) + 6H_2O\ (l)$$

Hydrogen peroxide is then employed to oxidize cobalt from +2 to +3 :

$$2[Co\ (en)_3]^{2+}\ (aq) + H_2O_2\ (aq) + 2H^+\ (aq) \longrightarrow 2[Co\ (en)_3]^{3+}\ (aq) + 2H_2O\ (l)$$

A cobalt (II) salt in ammonia (in presence of NH_4Cl) can be oxidized by air also.

For chromium, it is the +3 oxidation state that is commonly available. Thus, Cr (II) complexes can be made by reduction of Cr (III). This is commonly carried out with zinc amalgam (Zn/Hg) :

$$2\ \underset{\text{(Violet)}}{[Cr(H_2O)_6]^{3+}}\ (aq) + Zn/Hg \longrightarrow 2\ [Cr(H_2O)_6]^{2+}\ (aq) + Zn^{2+}(aq)$$

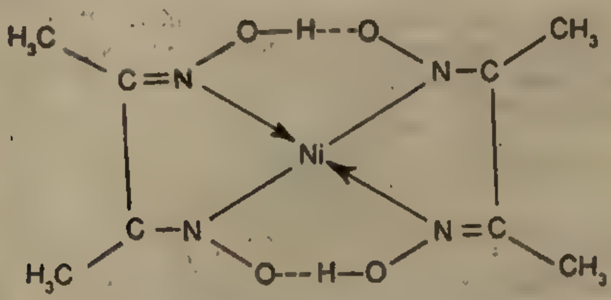
Once $[Cr(H_2O)_6]^{2+}$ is obtained, other complexes can be made by substituting other ligands for the water.

12·2·3. Properties of Coordination Compounds

Coordination compounds of transition metals are generally coloured. Some of the coordination compounds exhibit paramagnetic behaviour (presence of unpaired electrons). Many of the compounds possess conducting properties. Electrical conductance measure-

ments of coordination compounds in solution often indicate the number of ionic species present.

The intensity of visible radiation absorbed by a complex relates to the concentration of the complex in solution. Hence, the intensity of absorption can be used to estimate the amount of metal present in solution. Certain ligands are specific in their ability to form insoluble complexes with a metal, *e.g.* DMG forms with nickel ions a red rose coloured insoluble complex, which enables the concentrations of nickel to be estimated.



bis (Dimethylglyoximato) nickel (II)
(Insoluble in water)

The absorption spectra of a coordination compounds often indicate the nature of the metal ion, its oxidation state, coordination number of the metal ion, and the nature of the ligands.

12·3. NOMENCLATURE OF COORDINATION COMPOUNDS

Coordination compounds require systematic nomenclature to cope with the naming of the wide variety of possible compounds. The rules recommended by the Inorganic Nomenclature Committee of the International Union of Pure and Applied Chemistry (IUPAC) are given below :

(*i*) The cationic part (or positive part) of the coordination compound is named first, then the anion, *e.g.*.

$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (II)
$[Ag(NH_3)_2]Cl$	Diamminesilver (I) chloride
$K_3[Co(NO_2)_6]$	Potassium hexanitrocobaltate (III)

(*ii*) Ligands are named in alphabetic order regardless the number of each. The name of a ligand is treated as a unit. Thus 'diammine' is listed under '*a*' and 'dimethylamine' under '*d*'. Anionic names generally end in *-o*. In general, if the anionic ligand name ends in ide, ite or -ate, the final '*e*' is replaced by "*o*" giving -ido, -ito or -ato respectively.

Some of the anions do not follow the rule and their different versions are used, *i.e.*, fluoro (F^-), chloro (Cl^-), bromo (Br^-), iodo (I^-), oxo (O^{2-}), hydrido (H^-), hydroxo (OH^-), cyano (CN^-), *etc.*

$K[PtCl_3(C_2H_4)]$	Potassium trichloro (ethylene)-platinate (II).
$[Co(en)_2Cl_2]Cl$	Dichlorobis (ethylenediamine) cobalt (III) chloride.

Neutral ligands have their regular names except that H_2O is named 'aqua' (formerly aquo) NH_3 'ammine', NO 'nitrosyl' and CO, 'carbonyl'. Examples,

$[Cr(H_2O)_6]Cl_3$	Hexaaquachromium (III) chloride
$K_3[Fe(CN)_5CO]$	Potassium carbonylpentacyano ferrate (II).

Cationic ligand, which are rare, end with -ium.

(*iii*) If the metal atom is a part of the catonic part, the ligands are named first followed by the central metal. Di—, tri—, tetra—, *etc.* are used as prefixes to indicate the numbers of 'simple ligands ; bis, tris, tetrakis, *etc.* as used are prefixes for more complex ligands or when the ligand name contains the usual prefixes, *i.e.* di-, tri-, *etc.* Examples.

$NH_4[Cr(NCS)_4(NH_3)_2]$	Ammonium diammine—tetrakis (isothiocyanato)—chromate (III).
$[Pt(NH_3)_4(NO_2)Cl]SO_4$	Tetraamminechloronitroplatinum (IV) sulphate

(*iv*) The ending of the name of a complex anion is '-ate'.

$K_3[Cr(C_2O_4)_3]$	Potassium trioxalatechromate (III)
$K_2[CuCl_4]$	Potassium tetrachlorocuprate (II)
$Na_2[Fe(CN)_5NO]$	Sodium pentacyanonitrosylferrate (III)

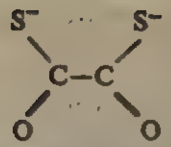
If the complex is neutral or cationic no ending is used. Examples.

$[Cu(en)_2]SO_4$	Bisethylenediaminecopper (II) sulphate
$[CoCl_3(NH_3)_3]$	Trichlorotriammine cobalt (III).

(*v*) The oxidation state of the central atom is indicated with a Roman numeral in parenthesis following the name of the metal. Examples

$[Fe(CO)_5)$	Pentacarbonyliron (0)
$Ba[BrF_4]_2$	Barium tetrafluorobromate (III)
$[Co(NH_3)_6][PtCl_6]$	Hexa ammine cobalt (II) hexachloro-platinate (IV)

(*vi*) Ligands with more than one donor atoms, may be denoted by adding the symbol for the atom or atoms through which attachment occurs at the end of the name of the ligand. For example, the dithiooxalate anion,



may be attached through S or O, and these are distinguished as dithiooxalato -SS′ and dithioooualato -OO′, respectively.

In some of the cases, different names are already used for different metals of attachment, *e.g.*, thiocyanto (-SCN) and isothiocyanato (—NCS), nitro (—NO_2) and nitrito (—ONO).

(*vii*) There are compounds in which a ligand acts as a bridge between similar or dissimilar metal ions and polymeric coordination compounds also exist.

Bridging ligands are prefixed by the Greek letter μ, *e.g.*,

$[(NH_3)_5\ Cr—OH—Cr(NH_3)_5]Cl_5$

μ—Hydroxobis[pentaamminechromium (III)] chloride

Exercise 12·1. Write down the formulae of the following coordination compounds.

(*i*) Chloropentaamminecobalt (III) chloride.
(*ii*) Tetraamminedichlorocobalt (III) chloride.
(*iii*) Tetrakis(pyridine)platinum (II) tetrachloroplatinate (II)
(*iv*) Triamminetrichlorochromium (III).
(*v*) Diamidotetraamminecobalt (III) ethoxide.
(*vi*) Potassiumdicyano bis (oxalato) nickelate (II).

Solution. (*i*) $[CoCl\ (NH_3)_5]Cl_2$.
(*ii*) $[Co\ (NH_3)_4\ Cl_2]Cl$.
(*iii*) $[Pt(py)_4]\ [PtCl_4]$.
(*iv*) $[Cr(NH_3)_3\ Cl_3]$.
(*v*) $[Co(NH_2)_2(NH_3)_4]OC_2H_5$.
(*vi*) $K_4[Ni(CN)_2(OX)_2]$.

Exercise 12·2. Name the following coordination compounds using IUPAC names :

(*i*) $[Co(en)_2\ Br_2]Cl$.
(*ii*) $K_3[Fe(CN)_6]$.
(*iii*) $[Ni(CO)_4]$.
(*iv*) $[Co(NH_3)Cl\ (en)_2]^+$.
(*v*) $[Ni(CN)_4]^{2-}$.
(*vi*) $[Cu(NH_3)\ (H_2O)Br_2]$.

Solution. (*i*) Dibromobis(ethylenediamine)cobalt (III) chloride.

(*ii*) Potassium hexacyanoferrate (III).
(*iii*) Tetracarbonylnickel (0).
(*iv*) Aminechlorobis (ethylenediamine)cobalt (III) ion
(*v*) Tetracyanonickelate (II) ion.
(*vi*) Ammineaquadibromocopper (II).

12·4. ISOMERISM IN COORDINATION COMPOUNDS

When two different compounds have the same molecular formula, but differ in the way that their atoms are arranged, they are said to be **isomers** of one another. Because of the fixed positions of the ligands in coordination compounds, several types of isomers are formed. Both structural isomers and steroisomers are possible.

12·4·1. Structural Isomerism

Structural isomers have different sets of bonds within the molecule.

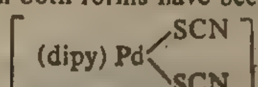
1. **Ionization Isomerism :** Complexes which have same stoichiometric composition but produce different ions in solution are known as ionization isomers and the phenomenon is ionization isomerism. For example,

$[Co(NH_3)_5Br]SO_4$ (dark violet), and
$[Co(NH_3)_5SO_4]\ Br$ (violet-red).

In solution, first one yields the ions $[Co(NH_3)_5Br]^{2+}$ and SO_4^{2-} whereas second one produces $[Co(NH_3)_5SO_4]^{+}$ and Br^- A similar set of examples is,

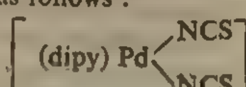
trans—$[Co(en)_2Cl_2]\ NO_2$ (green), and
trans—$[Co(ent)_2Cl\ NO_2]\ Cl$ (red)

2. **Structural Isomerism (or Linkage Isomerism) :** This type of isomerism occus when the monodentate coordinating groups have more than one donor sites (ambidentate ligands). Such groups are NCS^-, CN^-, NO_2^-, *etc*. Some examples of linkage isomers in which both forms have been isolated, are as follows :

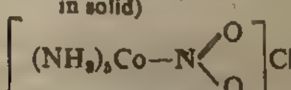


Dipyridyldithiocyanato-palladium (II)
(Stable at room temperature in solid)

and

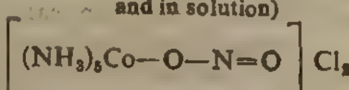


Dipyridyldiisothiocyanato-palladium (II)
(Stable at elevated temperatures and in solution)



Pentaammine nitro cobalt (III) chloride
(Yellow-brown, stable in acids)

and



Pentaamminenitrocobalt (III) chloride
(Red, unstable in acids)

3. **Coordination Isomerism.** This type of isomerism can occur in compounds containing both complex cations and complex anions. Such isomers involve exchange of ligands between cation and anion, *i.e.*, between coordination spheres.

A set of examples is

$[Co^{III}(NH_3)_6][Cr^{III}(CN)_6]$ and $[Cr^{III}(NH_3)_6][Co^{III}(CN)_6]$

Hexaammine cobalt (III) hexacyanochromate (III) — Hexaammine chromium (III) hexacyanocobaltate (III)

A total of 12 isomers of this complex are possible. In the above examples different metal ions are present as cations and anions. In some cases the same metal ion with different distribution of donor components, can also appear in both cation and anion, for example,

$[Cr^{III}(NH_3)_6]\ [Cr^{III}(CNS)_6]$ and
$[Cr^{III}(NH_3)_4(CNS)_2]\ [Cr^{III}(NH_3)_2(CNS)_4]$.

Sometimes the same metal which appears in both cation and anion may have different oxidation states, *e.g.*,

$[Pt^{II}(NH_3)_4]\ [Pt^{IV}Cl_6]$ and
$[Pt^{IV}(NH_3)_4Cl_2]\ [Pt^{II}Cl_4]$.

4. **Hydrate Isomerism.** Hydrate isomerism and ionization isomerism are quite similar. This type of isomerism arises due to different positions of water molecules, inside and outside the coordination sphere of complexes of the same empirical formula. The classical example of this type is $CrCl_3.6H_2O$ as shown below :

$[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (green)
Tetra aquadichloro chromium (III) chloride dihydrate
$[Cr(H_2O)_5Cl]\ Cl_2.H_2O$ (blue green)
Pentaaquachlorochromium (III) chloride hydrate
$[Cr(H_2O)_6]Cl_3$ (violet)
Hexaaqua chromium (III) chloride

Green form upon dilution with water produces first the blue-green isomer and finally the violet one. Another example of this type is :

$[Co(NH_3)_4(H_2O)Cl]Cl_2$
Tetraammine aquachlorocobalt (III) chloride
and $[Co(NH_3)_4Cl_2]\ Cl.H_2O$
Tetraamminedichlorocobalt (III) chloride hydrate

12.4.2. Stereoisomerism

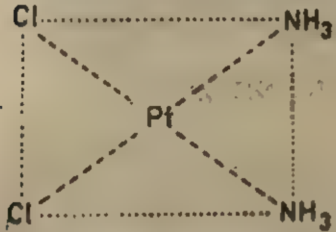
This isomerism arises due to different arrangements of atoms or groups in space in molecule. Sometimes it is called space isomerism. This type of isomerism is more common in complexes of coordination number 4 and 6. Stereoisomerism is of two types : 1. Geometrical isomerism, 2. Optical isomerism.

1. **Geometrical Isomerism.** When two identical ligands occupy adjacent positions the isomer is called cis (cis means same in Latin), and when arranged opposite to each other, the isomer is called trans (trans means across in Latin). Cis-trans isomerism is quite common in octahedral and square planar complexes but not possible for complexes with coordination numbers 2 and 3 and tetrahedral complexes with 4 coordination number.

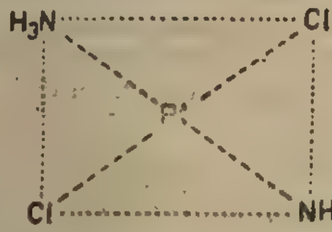
In tetrahedral complexes, all ligands are adjacent to each other, hence, they do not show any geometrical isomerism.

Square Planar Complexes. Cis-trans isomerism for the square planar complexes of the type Ma_2b_2, Ma_2bc and Mabcb (where M=metal ion and a, b, *etc.*=different monodentate ligands) is possible.

(*i*) **Ma_2b_2 type complexes.** Three examples of this type of complexes are $[Pt(NH_3)_2Cl_2]$, $[Pd(NH_3)_2(NO_2)_2]$ and $[PtCl_2(py)_2]$. Cis-trans isomers of $[Pt(NH_3)_2Cl_2]$ are shown below :

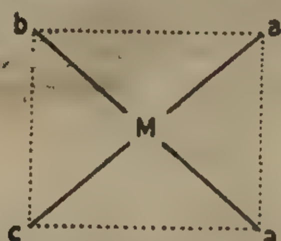


cis-diamminedichloro-platinum (II)
(pale yellow, insoluble in water)

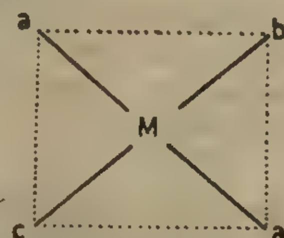


trans-diamminedichloro-platinum (II)
(dark yellow, water soluble)

(*ii*) **Ma_2bc type complexes.** Examples of this type may occur in either of the followings forms :



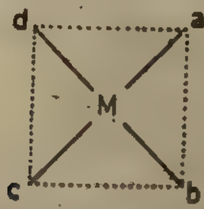
cis



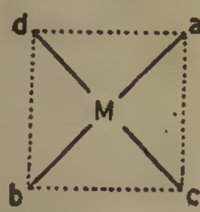
trans

An example of this type of complex is $(PtCl(NH_3)(py)_2]$.

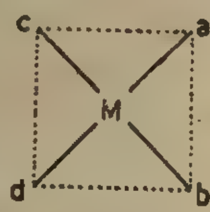
(*iii*) **Mabcd type complexes.** The possible isomeric forms of this type of complex are :



trans, a–c



trans, a–b



trans, a–d

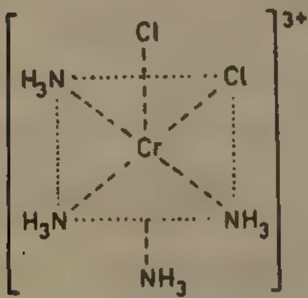
An interesting example of this type of complex is
$[Pt(NH_3)(py)Cl\ Br]$.

Octahedral Complexes. These complexes may exhibit both position and optical isomerism in certain formula types.

Complexes of the formula type Ma_6 or Ma_5b (a or b is a monodentate ligand) do not exhibit stereoisomerism.

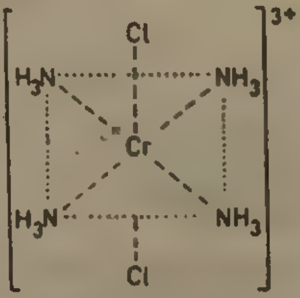
(*i*) **Ma_4b_2 type complexes.** Example of this type can exist only in the cis-trans isomeric forms.

A common example of this type is $[Cr(NH_3)_4\ Cl_2]^{3+}$



(Two chloro groups are in cis-position)

Tetraammine-cis-dichloro-chromium (III) ion (violet)

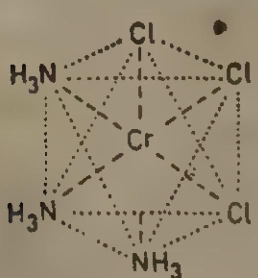


(Two chloro groups are in trans-position)

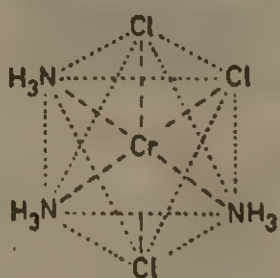
Tetraammine-trans-dichloro chromium (III) ion (green)

Antoher example is $[Co(NH_3)_4(NO_2)_2]^+$..

(*ii*) **Ma_3b_3 type complexes.** A few isomers of type Ma_3b_3 are known. The two forms of the complex $(Cr(NH_3)_3\ Cl_3]$ are,



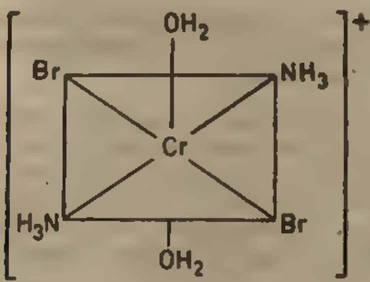
cis-trichloro triammine-chromium (III)



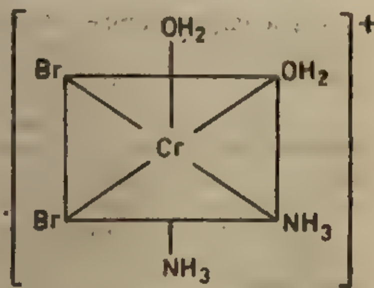
trans-trichloro triammine chromium (III)

(*iii*) **$Ma_2b_2c_2$ type complexes.** These type of complexes exhibit several isomeric forms.

A typical example of this type is $[Cr(H_2O)_2(NH_3)_2Br_2]^+$. Each of the like ligands may be trans to each other or cis to each other.

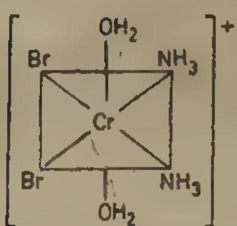


trans-diammine-trans-diaqua-trans-dibromochromium (III) ion

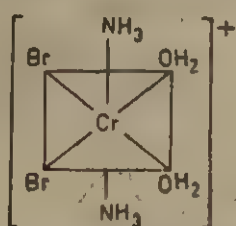


cis-diammine-cis-diaqua-cis-dibromochromium (III) ion

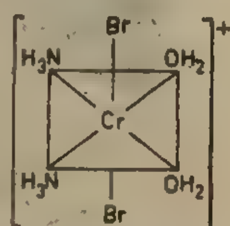
One pair of ligands may be trans to each other, but the others cis.



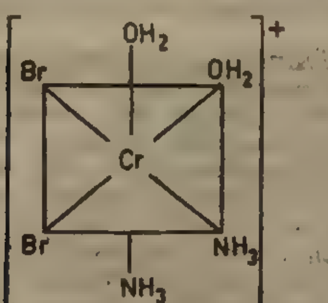
cis-diammine-trans-diaqua-cis-dibromo-chromium(III) ion

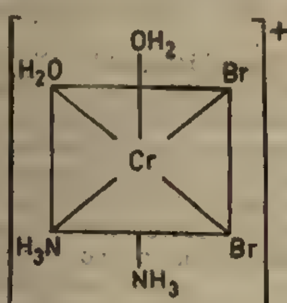


trans-diammine-cis-diaqua-cis-dibromo-chromium (III) ion



cis-diammine-cis-diaqua-trans-dibromo-chromium (III) ion





Optical isomers of cis-diammine-cis-diaqua-cis-dibromochromium (III) ion

On further interchanging the positions of the ligands, no new geometric isomers are produced. However, one of the five geometric isomers (cis to one like itself) can exist in two distinct forms called optical isomers as shown on page 655.

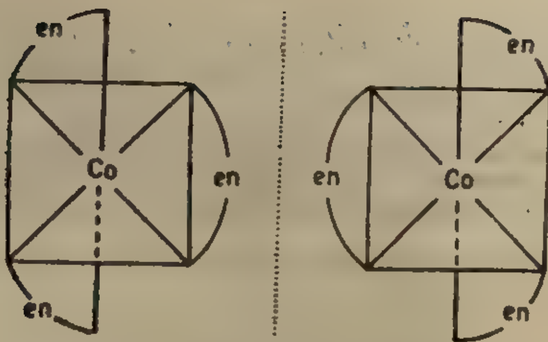
The largest number of geometrical isomers would exist for a complex of the type Mabcdef, wherein each monodentate ligand is different, *e.g.*, $[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$

2. **Optical Isomerism.** Optical isomerism arises in molecules with an asymmetric centre on the ligand or a general asymmetry in the complexes. Isomers exist in two forms and bear the same structural relationship to each other as left and right hands, *i.e.*, the two isomeric forms are non-superimposable mirror images of one another (Fig. 12·1) and are called optical isomers or **enantiomers.**

Fig. 12.1. Illustration of non-superimposable mirror images.

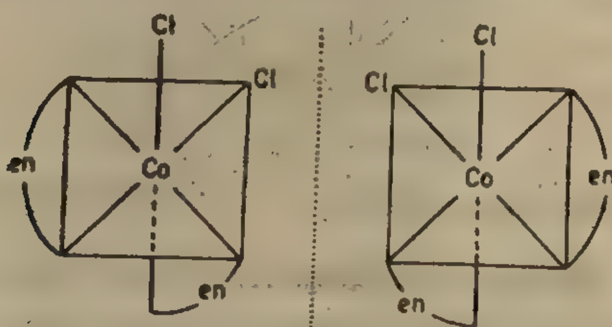
Optical isomers have identical physical and chemical properties except that they interact with polarized light in different ways. Separate equimolar solutions of two isomers will rotate a plane of polarized light by equal amounts in opposite directions. When an optical isomer rotates the plane of polarized light to the right, it is called dextrorotatory (dextro or *d*) isomere, and when it rotates to the left, it is laevorotatory (laevo or *l*) isomer. The presence of a bidentate ligand in a complex can increase the possibility of optical isomerism. Octahedral complexes of the type $[M(aa)_3]$, $[M(aa)_2b_2]$ $[M(aa)b_2c_2]$ where b or c is a monodentate ligand, aa is a symmetrical bidentate ligand.

(*i*) **$M(aa)_3$ type complex :** An example of this is the complex ion, tris-(ethylene diammine) cobalt (III) ions.



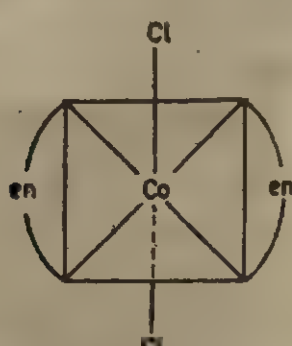
d- and l-forms of $[Co(en)_3]$

(Two configurations related as object and mirror image). Other examples are $[Cr(C_2O_4)_3]^{3-}$, $[Pt\ (en)_3]^{4+}$ *etc.* ions.



(a) (b)

cisforms (optical isomers) $[Co(en)_2Cl_2]$.

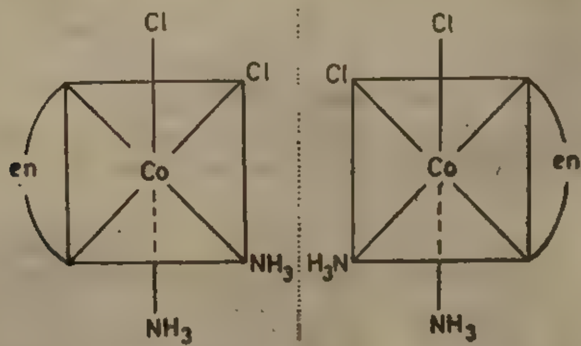


(c)

transform of $[Co(en)_2Cl_2]^+$

(*ii*) **$M(aa)_2b_2$ type complex :** An example of this is the complex ion, dichlorobis(ethylenediamine) cobalt (III) ion, $[Co(en)_2 Cl_2]^+$. The ion has two cis isomers (a, b) which are also optical isomers and one trans (c) isomer.

(*iii*) **$M(aa)b_2c_2$ type complex :** These complexes also exist in three forms, two are optically active and the third one is optically inactive. Examples are $[Co(en)(NH_3)_2Cl_2]^+$ and $[Co(C_2O_4)(NH_3)_2 (NO_2)_2]$.



Optical isomerism is rarely observed in square planar complexes.

12.5. BONDING IN COORDINATION COMPOUNDS

Bonding theories for coordination compounds should be able to account for structural features, colours and magnetic properties. Three theories to explain the bonding in complexes, are the valence bond theory, crystal field theory (and its modification ligand field theory) and the molecular orbital theory.

Valence Bond Theory (VBT)

This theory accounts for structural and magnetic properties but offers no explanation for the wide range of colours of coordination compounds. This is the simplest of all the theories and involves the classical picture of the chemical bond. It was introduced in 1931 by Linus Pauling. According to this theory, the metal cation furnishes a set of empty orbitals, eqnal to it coordination number which, in turn, hybridize to form a new set of equivalent hybridized orbitals, while the ligand furnishes the electron pairs for bond formation. Hybridized atomic orbitals (empty) of the metal overlap with the filled orbitals of the ligands to accept lone pairs of electrons and, in turn, to form covalent bonds. The theory also assumes the pairing up of unpaired electrons and thus making available of o:bitals for hybridization.

Accordingly, suitable hybridized orbitals are formed on the metal ion by involving the empty s, p and d orbitals. In cases, where the d orbitals are completely filled (or completely empty or not available only s and p orbitals are involved in the formation of metal orbitals. Each set of hybridized orbitals gives rise to the directional bonds in a stable gemoetrical arrangement around metal ion depending on the type of orbitals used. The different types of hybrids involved in the formation of coordinate bonds and the corresponding geometry assumed by them is given in Table 12.3.

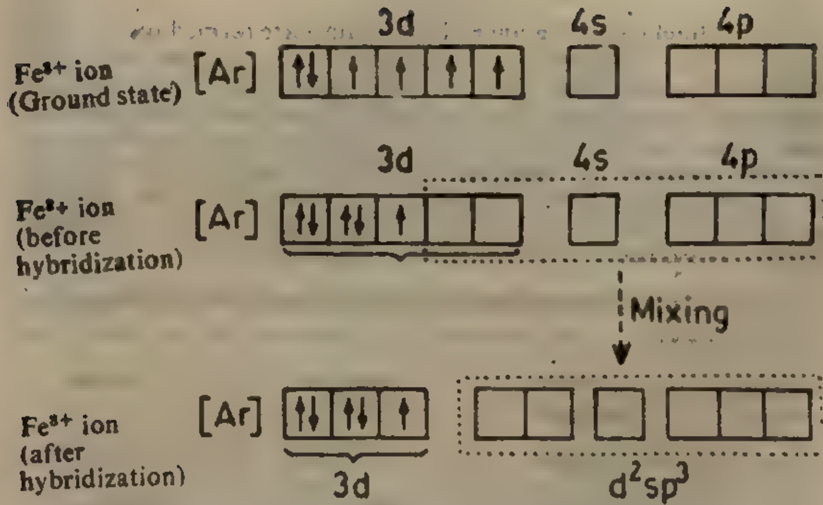
TABLE 12.3 Possible molecular geometry of various hybrid orbital systems

Coordination number	*Orbitals hybridized*	*Molecular geometry*	*Example*
2	sp	linear	$[Ag(NH_3)_2]^+$
3	sp^2	trigonal	$[HgI_3]^-$
4	sp^3	tetrahedral	$[Zn(NH_3)_4]^{2+}$
4	dsp^2	square planar	$[Ni(CN)_4]^{2-}$
5	dsp^3	triagonal bipyramid	$[CuCl_5]^{3-}$
6	d^2sp^3	octahedral	$[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
6	sp^3d^2	octahedral.	$[CoF_6]^{3-}$ $[FeF_6]^{3-}$

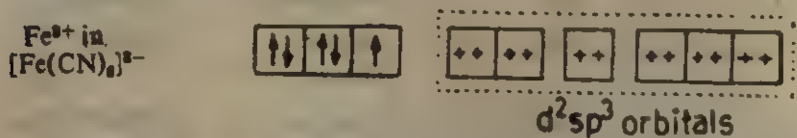
Now let us take some examples of coordination compounds to explain the valence bond approach. Hexa cyano ferrate (III) ion is known to be paramagnetic (corresponding to one electron) and octahedral. The valence bond description of the bonding in $[Fe(CN)_6]^{3-}$ ion is as follows :

		3d					4s	4p		
Iron atom (Ground state)	[Ar]	↑↓	↑	↑	↑	↑	↑↓			

The Fe^{3+} is formed upon ionization of the 4s electrons and one of 3d electrons.



Each of six CN^- ligands now donates two electrons into one of the six d^2sp^3 oritals forming the six coordinate covalent bonds. The bonding arragement illustrates one unpaired electron and is therefore paramagnetic.



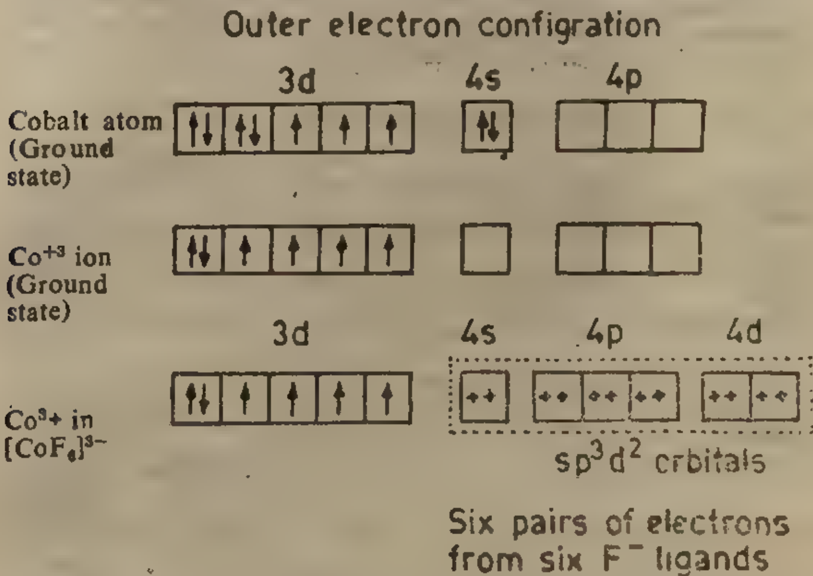
Six pairs of electrons from six CN^- ligands

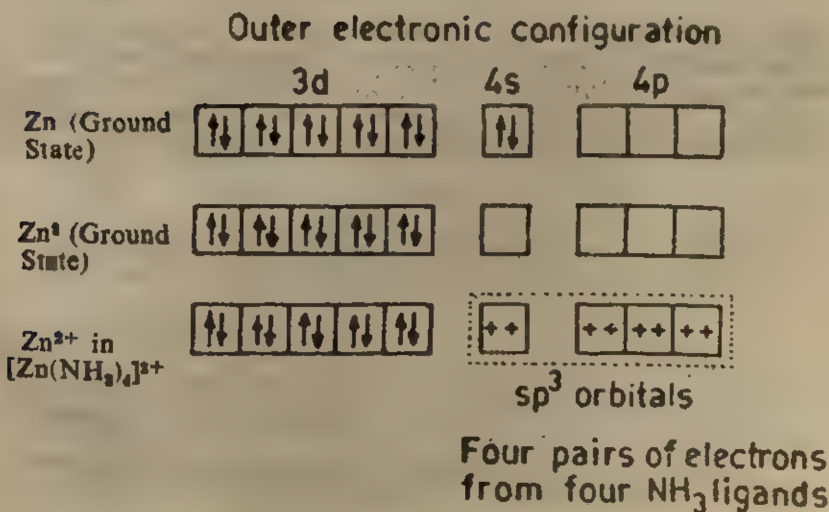
The d^2sp^3 orbitals have been shown by quantum mechanics to be octahedral hybrids. Fig. 12·2 shows the overlap of the six

Fig. 12.2. The octahedral $[Fe(CN)_6]^{3-}$ ion

d^2sp^3 hybrid orbitals of Fe^{3+} with the six CN^- ligand orbitals to form six bonds and a resulting octahedral structure.

The hexafluorocobaltate (III)i on involves $sp^3\ d^2$ hybridization. This complex is octahedral with the measured magnetic moment corresponding to four unpaired electrons. In this case, the field of F^- is not sufficient to pair up electrons in the inner d orbitals but just sufficient to give sp^3d^2 hybrid orbitals by utilising two of the outer 4d empty orbitals. The structure is explained as suggested below :

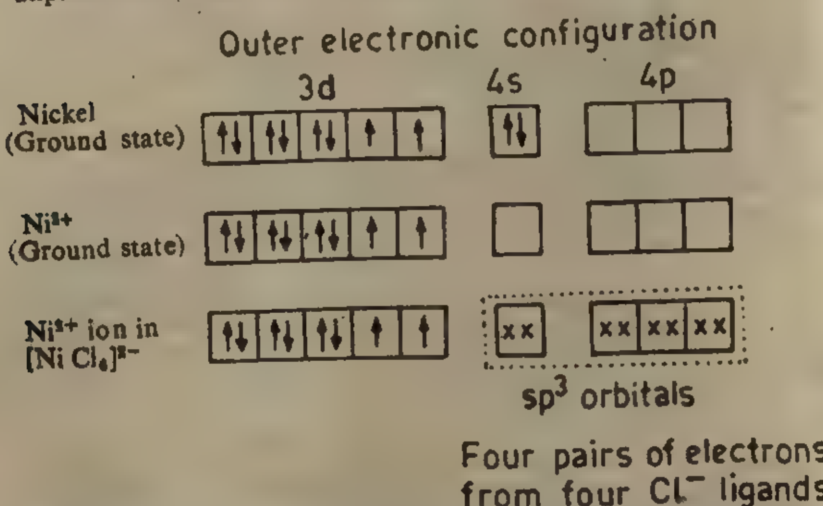




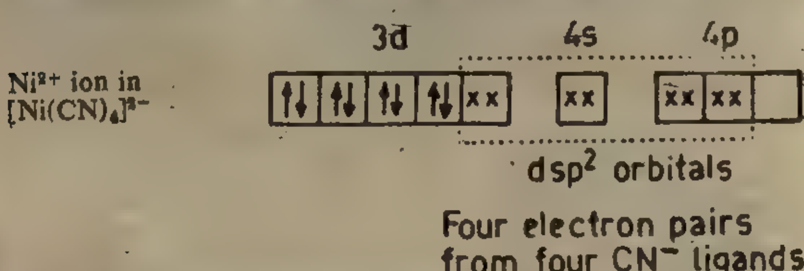
Most complexes with coordination number four are either tetrahedral or square planar. Tetrahedral geometry results from sp^3 hybridization. Group 12 metals (Zn, Cd, Hg) in their +2 oxidation form tetrahedral complexes since they all have d^{10} configurations. Tetraammine zinc ion, for example, is diamagnetic and tetrahedral.

Since Cu^+ is also d^{10} ion, this also adopts tetrahedral structure in $[Cu(CN)_4]^{3-}$. It is diamagnetic in nature.

Complexes of a few other trasition metal ions are also tetrahedral. For example, $[NiCl_4]^{2-}$ is paramagnetic with two unpaired electrons, and is tetrahedral.



$[Ni(NH_3)_4]^{2+}$ ion also adopts tetrahedral structure. Pauling's theory cannot account for these if observations. On the other hand, when Ni^{2+} forms $[Ni(CN)_4]^{2-}$ the result is a diamagnetic square planar structure. The two umpaired 3d electrons become paired, making available one d orbital for hybridization in a dsp^2 complex.



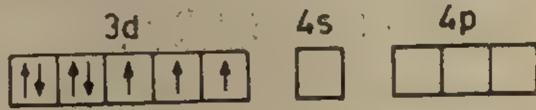
The metal ions most commonly forming square planar complexs are Cu (II), Au (III), Co (II), Pt (II), *etc.* In the complex

$[Ni(CN)_4]^{2-}$, the CN^- ligand is strong and it compels the two unpaired electrons to pair up. As a result one 3d orbital becomes available which participates in dsp^2 hybridization.

Exercise 12.3. The $[CoCl_4]^{3-}$ is paramagnetic in nature. What is its geometry ? Paramagnetism corresponds to more than one electron.

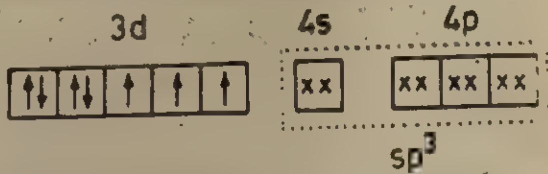
Solution. The oxidation state of cobalt in the complex ion is +2 and hence Co^{2+} is d^7.

Co^{2+} ion



As the value of paramagnetism corresponds to more than one electrons, the ion should adopt tetrahedral geometry.

Co^{2+} ion in $[CoCl_4]^{2-}$

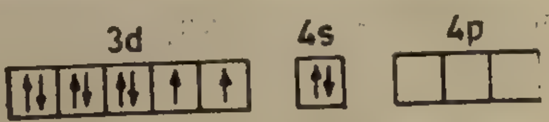


Therefore the complex ion is tetrahedral and has three unpaired electrons.

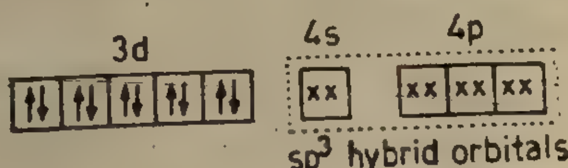
Exercise 12.4. The complex $Ni(CO)_4$ adopts tetrahedral structure but $[Ni(CN)_4]^{2-}$ adopts square planar geometry. Comment on the geometries of the two species.

Solution. Nickel metal is $3d^8\ 4s^2$. In $Ni(CO)_4$ nickel is zerovalent.

Nickel (ground state)



Ni under the influence of 4CO molecules



Under the influence of CO, the two 3d unpaired electrons become paired. Further the electrons occupying the 4s orbital also shift to 3d orbitals and make the space available for hybridization in a sp^3 complex. The structure is, therefore, tetrahedral. The molecule is diamagnetic.

On the other hand, $[Ni(CN)_4]^{2-}$ ion has square planar geometry and hence it involves dsp^2 hybrid orbitals. The species is diamagnetic as there is no unpaired electron.

Now, for coordination compounds, the valence bond theory has been replaced by crystal field theory. One of the main reasons for this was that the valence bond approach could not explain the colour (visible spectra) of coordination compounds. In addition, although valence bond model can explain the magnetic properties of many compounds, it does not satisfactorily provide a basis for a more quantitative treatment of paramagnetic compounds.

Another theory which has been extensively used in connection with coordination compounds is the crystal field theory (CFT). The theory does not consider the bond between ligand and metal to be covalent, sa does the valence bond model, but to be a purely ionic bond. Accordingly, the ligands represent either the negative charges or the negative ends of the dipoles directed toward the central metal atom or ion. The extent of the attractive forces determines the stability of the complex and is dependent on the charge and size of the central ion and ligands. The field of the coordinated ligands influences the ground state energy of the d orbitals of the metal, and thus, leads to destabilization and splitting of the energy levels. From the extent of splitting (that depends upon the nature of the metal ion and the ligands) the geometries and properties of the complexes have been explained.

The ligand field theory an outgrowth of crystals field theory, considers the contribution of covalent bonding between the metal and the ligands.

12.6. STABILITY OF COORDINATION COMPOUNDS IN SOLUTION

A metal ion in aqueous solution does not exist simply as M^{n+} but as an aqua complex $[M(H_2O)_x]^{n+}$ when a ligand, L is added to the solution, some or all of the coordinated water is replaced by the ligands.

$$[M(H_2O)_x]^{n+} + xL \rightleftharpoons [M(L)_x]^{n+} + xH_2O$$

The replacement of water occurs in steps; the successive equilibria may be represented as

$$M^{n+} + L \rightleftharpoons [ML]^{n+} \qquad k_1 = \frac{[ML]^{n+}}{[M^{n+}][L]}$$

$$[ML]^{n+} + L \rightleftharpoons [ML_2]^{n+} \qquad k_2 = \frac{[ML_2]^{n+}}{[ML]^{n+}[L]}$$

$$[ML_2]^{n+} + L \rightleftharpoons [ML_3]^{n+} \qquad k_3 = \frac{[ML_3]^{n+}}{[ML_2]^{n+}[L]}$$

$$\vdots \qquad\qquad\qquad \vdots$$

$$ML_{x-1} + L \rightleftharpoons ML_x \qquad k_x = \frac{[ML_x]^{n+}}{[ML_{x-1}]^{n+}[L]}$$

where k_1, k_2, k_3, $\cdots k_x$ represent the stepwise formation (stability) constants. When we consider the overall equilibrium, the overall stability constant, K is given as

$$M^{n+} + xL \rightleftharpoons ML_x \qquad K = \frac{[ML_x]^{n+}}{[M^{n+}][L]^x}$$

It is customary to omit the coordinated water molecules from the equilibrium equations.

Considering the charge on the ligand, K is given as

$$M^{n+} + xL^{m-} \rightleftharpoons \frac{[ML_x]^{z+}}{[M^{n+}][L^{m-}]^x}$$

where $z-$, $m-$ are the charges carried by the complex and ligand respectively. To balance charges, it is required that

$$(n+) + x(m-) = (z+)$$

x is the coordination number of the metal.

From the stability constant expression, it is evident that, the stability of complexes is a function of a number of factors involving both metal and ligand. The oxidation state, size, and electron configuration of the metal ion affect the stability of a complex. The size of the ligand, its charge and the size and number of chelate rings also affect the stability of a complex. On the basis of data available, it is borne out that the stability of the complexes formed by one group of metals and a certain ligand usually increases as the size of the metal increases. The values of stability constants for some complexes are given in Table 12·4.

TABLE 12.4. Stability constants for some complexes (or ions) at 298K

Complex species	*Stability constant, K*
$[Ag(CN)_2]^-$	1×10^{21}
$[AgCl_2]^-$	$1{\cdot}11 \times 10^5$
$[Ag(NH_3)_2]^+$	1×10^8
$[Cu(NH_3)_4]^{2+}$	1×10^{13}
$[Cu(CN)_4]^{3-}$	2×10^7
$[Fe(CN)_6]^{4-}$	1×10^{24}
$[Fe(CN)_6]^{3-}$	1×10^{42}
$[Co(HN_3)_6]^{3+}$	5×10^{33}
$[Co(NH_3)_6]^{2+}$	$1{\cdot}11 \times 10^5$
$[Ni(CN)_4]^{2-}$	1×10^{30}
$[Ni(NH_3)_6]^{2+}$	6×10^8
$[Zn(CN)_4]^{2-}$	1×10^{17}
$[Zn(NH_3)_4]^{2+}$	3×10^9

From the Table 12.4 on stability constant values of complexes, some conclusions can be made :

1. Stability constants depends upon the nature of the metal and ligand.

2. When a metal ion with different oxidation states forms complexes with the same ligand, the complex with a higher oxidation stable (or the smaller the size) is always more stable.

3. The more basic a ligand, the greater is the ease with which it can donate its lone pair of electrons, and therefore, the greater is the stability of the complexes formed by it. Thus Cn^-, F^- and NH_3 species are strong bases, *i.e.* good ligands and form many stable complexes. For anionic ligands, the higher the charge and the smaller the size, the more stable is the complex formed. Thus F^- ion gives more stable complexes then does Cl^- ion.

12.7. IMPORTANCE OF COORDINHTION COMPOUNDS

The tendency of metals to form complexes with ligands and their stability plays an important role in a variety of situations Complexes find wide use in analytical chemistry, bio-chemical systems, industries, electroplating, water treatment, soil and plant treatment, *etc.*

Analytical Chemistry. A test for the detection of Cu(II) involves the formation of deep blue coloured complex on the addition of ammonia (excess) to a solution of Cu (II) salt.

$$Cu^{2+} + 4NH_3 \longrightarrow \underset{\substack{\text{Tetraammine cupper (II) ion} \\ \text{(Blue colour)}}}{[Cu(NH_3)_4]^{2+}}$$

Brown complex, $Cu_2[Fe(CN)_6]$ formation is another test employed for the purpose.

$$2\,Cu^{2+} + [Fe(CN_6]^{4-} \longrightarrow \underset{\text{(Brown precipitate)}}{Cu_2[Fe(CN)_6]}$$

To separate silver ion from the precipitate of AgCl, Hg_2Cl_2 and $PbCl_2$ formed in Group I, aqueous ammonia is added when AgCl dissolves due to formation of the complex ion.

$$Ag^+ + 2\,NH_3 \longrightarrow \underset{\text{(Soluble)}}{[Ag(NH_3)_2]^+}$$

Hg_2Cl_2 and $PbCl_2$ do not form complexes and therefore do not dissolve.

Dimethylglyoxine is an example of chelating agent and used in obtaining an insoluble scarlet-red precipitate. This precipitate is used to detect and estimate nickel ions.

$$Ni^{2+} + 2\,DMGH_2 \longrightarrow Ni(IMGH)_2 + 2H^+$$

Disodium salt of EDTA, a hexadentate ligand complexes numerous metal ions ; may even be used in titrimetric procedures. It is used in titrimetric estimation of Ca^{2+} and Mg^{2+} ions. This method is used to determine the hardness of water.

Metallurgical operations. In the extraction of silver and gold, the ores are treated with CN^- ions ; when metals form soluble cyano complexes. On treating the solution with zinc (an active metal), silver or gold is precipitated. The stability of the cyanide complex of metals results in an electrode potential sufficiently negative that oxygen can oxidize Ag and Au, which normally are quite rsistant to attack.

$$4M(s)+8CN^-(aq)+O_2(g)+2H_2O \longrightarrow 4[M(CN)_2](aq) +4OH^-(aq)$$

(M=Ag or Au)

$$2[M(CN)_2]^-+Zn \longrightarrow [Zn(CN)_4]^{2-}+2M(s).$$

Photography. The photographic fixing process depends on the formation of the soluble dithiosulphato silver (I) ion. The reduction of AgBr left on the developed negative produces a totally black film. To avoid this, the image is fixed ; the unreduced AgBr is removed by converting the silightly soluble salt into a soluble complex ion, using sodium thiosulphate

$$AgBr(s)+2\ S_2O_3^{2-}(aq) \longrightarrow \underset{\text{(Soluble)}}{[Ag(S_2O_3)_2]^{3-}}(aq)+Brf^-(aq)$$

Biological processes. Several coordination complexes have important biochemical roles. Chelates of tetradentate porphyzin ligands and magnesium (chlorophyll), iron (haeme) and cobalt (vitamin B_{12}) are the most significant.

The chlorophyll (Fig. 12·3), a green pigment found in plants, is a complex of magnesium (II) with macrocyclic ligands 'chlorin' (bold lines) derived from the parent tetrapyrrole molecule prophyrin (planar organic group). It acts as a catalyst in the coversion of carbon dioxide and water into carbohydrates. Since this process requires light, it is called photosynthesis.

$$6n\ CO_2+6nH_2O \xrightarrow[\text{Sunlight}]{\text{Chlorophyll}} (C_6H_{12}O_6)n$$

Haeme (Fig. 12.4) attached to protein (globin) in the blood, contains iron (II) bound to a large porphyrin ring. It is responsible for the transport of oxygen throughout the body.

The oxygen molecule becomes reversibly attached to the central iron Fe (III). The reddish colour of oxygen rich blood is due to this oxygen iron complex. Deoxygenated blood is darker and slightly bluish.

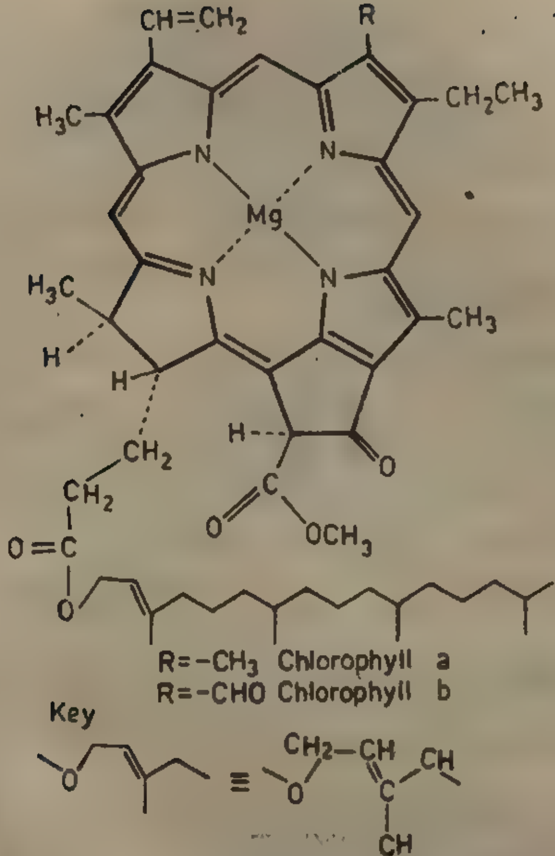


Fig. 12.3. Chlorophyll.

The sixth coordination position of iron atom is coordinated to a water molecule [tFig. 12·5 (*a*)] or to the oxygen molecule [Fig. 12·5 (*b*)]. The aquated haemoglolin (deoxyhaemoglobin) is a paramagnetic Fe (II) species while the oxygenated haemoglobin (oxychaemoglobin) is diamagnetic Fe (III) species.

Haeme and chlorophyll are remarkably similar in structure, a fact that may suggest a distant evolutionary entity that predates plants and amimals as such.

Vitamin B_{12} (Fig. 12·6) is the only vitamin that contains a metal ion at the centre of corrin ring (bold lines) system similar to the arrangement of iron (II) in haeme. It is a coenzyme needed in the formation red blood cells and in a number of other biochemical cells. The usual methods of isolation lead to a product known as

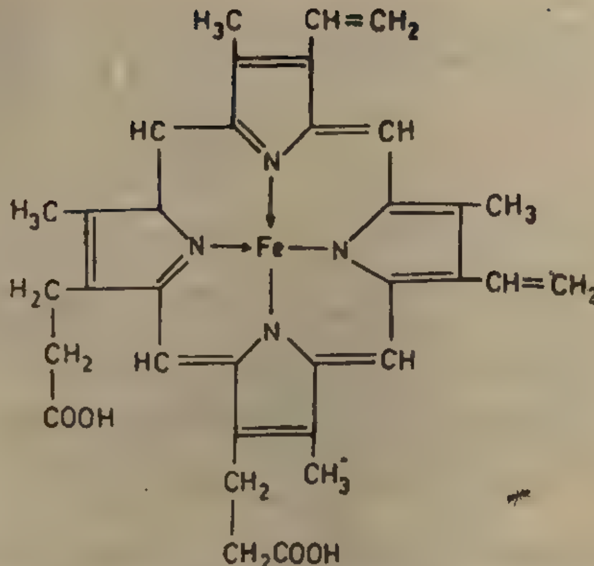
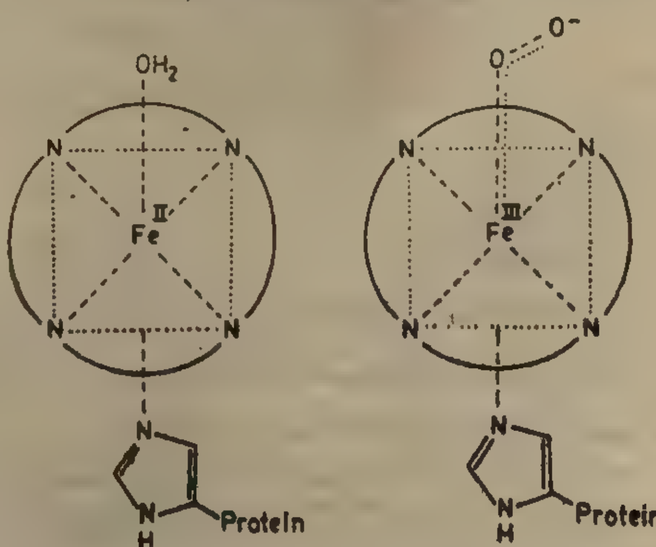


Fig. 12.4. Haeme, iron-porphyrin ring system complex.



(a) (b)

Fig. 12.5. (a) Prosthetic group (ferrohaeme) of haemoglobin water occupying the sixth coordination position.
(b) oxyheamoglobin ; oxygen complex of ferrohaeme.

cyano cobalamin, which is the same as vitamin B_{12} itself but with CN^- instead of deoxyadenosine in the sixth coordination position. It is used in the treatment of pernicious anaemia.

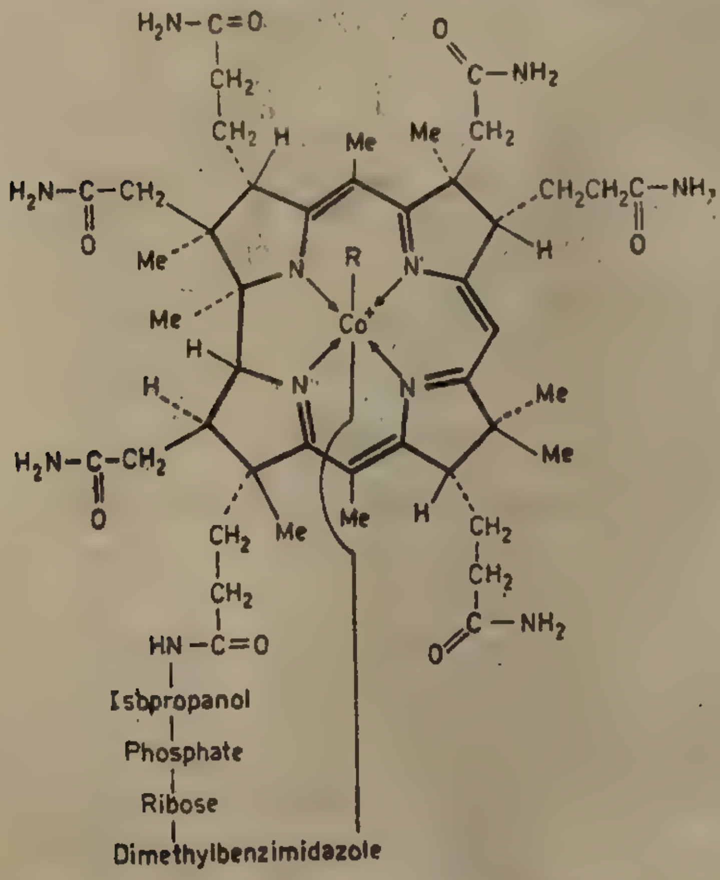


Fig. 12.6. Vitamin B_{12} (cyanocobalamin)

12.8. ORGANOMETALLIC COMPOUNDS

An organometallic compound is one in which a metal to carbon bond is formed. Compounds of elements such as boron, silicon, germanium, arsenic, antimony and tellurium are also included in this category.

Since the discovery of the alkyls of zinc and murcury over a century ago, many new compounds have been discovered. The discovery of Grignard reagents (organomagnesium halides) in 1900

proved to be a boon for a variety of organic synthesis. In 1951, Ferrocene, Fe $(C_2H_5)_2$ was discovered accidentaly. Its synthesis and structure opened up a new field of research (π complexes) in the organometallic chemisty of transition metals

Organometallic compounds may be clabssified on the nature of bonding :

1. **Ionic compounds.** The organo compounds of highly electropositive metals are usually ionic. Their stability depends upon the stability of carbanian. Compounds of unstable anions (*e.g.*, $C_2H_{2n+1}^-$) are generally highly reactive and often unstable. Salts of the type $(C_6H_5)_3\ C^-\ Na^+$ and $(C_5H_5)_2^-\ Ca^{2+}$ are more stable because of the delocalization of electrons. They are still reactive.

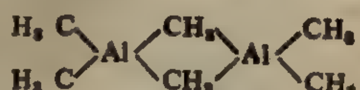
2. **σ-Bonded compounds.** In these compounds the organic reside is bound to a metal atom by a normal 2-electron covalent bond. Such compounds are formed by weakly electropositive metals, and of course by non-metallic elements.

For example,

R—Mg—X Grignard reagent X=halogen R=alkyl or aryl group	$(CH_3CH_2)_2Zn$ Diethyl zinc	$(CH_3)_4$ Sn Tetra methyl tin

$Al_2(CH_3)_6$

Trimethyl aluminium (dimer)



Two methyl groups act as bridges

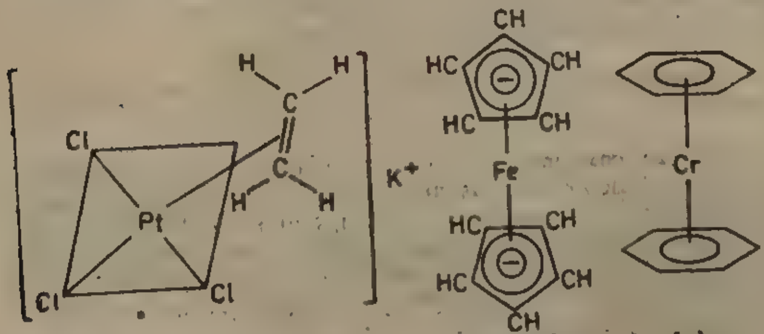
$(CH_3)_3$ Sn Cl
Trimethyltin chloride

(CH_3) Sn Cl_3
Methyltin trichloride

Most of the compounds in this category have predominantly covalent bonding and behave organic like. They differ in certain respects from carbon chemistry due to (*i*) possibility of using higher d arbital, *e.g.* in SiR_4 but not in CR_4, (*ii*) donar ability of alkyls or aryls with lone pairs as in PEt_3, and (*iii*) electron deficient nature of the metal as in BR_3 or coordinative unsaturation as in ZnR_2.

3. **π Bonded compounds.** Alkyls or aryls of transition metals are comparatively less stable than those of main group elements. Transition metal to carbon σ bonds also exist in nature in vitamin B_{12} derivatives. These metals form bonds with unsaturated hydrocarbons and other molecules. *i.e.*, bond with π-bonding ligands.

Some examples of π-complexes are shown in Fig. 12·7.



(a) $K[PtCl_3(\eta^2-C_2H_4)]Cl_3$ Zeisse's salt

(b) Ferrocene $Fe(\eta^5-C_5H_5)_2$

(c) Dibenzene chromium $Cr(\eta^6-C_6H_6)_2$

Fig. 12.7. π-complexes of transition metals.

The Greek letter eta (η) followed by a numeral in these compounds indicates the number of carbon atoms bound to the metal. Thus, the prefixes η^2, η^5 and η^6 represent that 2, 5, 6 carbon atoms are bound to the metal in Zeisse's salt, ferrocene and dibenzene chromium respectively.

The compound of unsaturated hydrocarbon and platinum was prepared by the Danish chemist Zeisse in 1927.

$$[PtCl_4]^{2-} \quad + \quad C_2H_4\,(aq) \longrightarrow [PtCl_3(C_2H_4)]^- \rightarrow$$

Anion of Zeisse's' salt

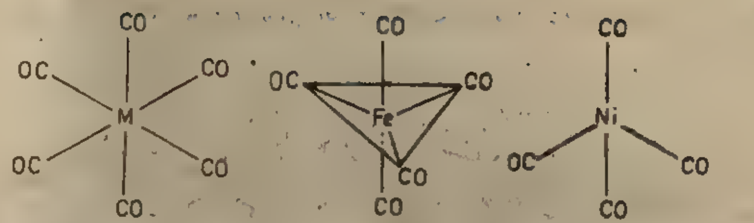
$[PtCl_2C_2H_4]_2^0$

(Extracted with ether)

Acetylene also forms such complexes with a limited group of metal ions : Rh(I), Ir (II), Pd(II), Pt (II), Cu (I), Ag (I), and Hg (II). The three metal ions, Cu (I), Ag(I) and Hg(II) have full d orbitals hence, the requirement of empty d orbitals on the metal are not necessary for binding the olefiin molecules.

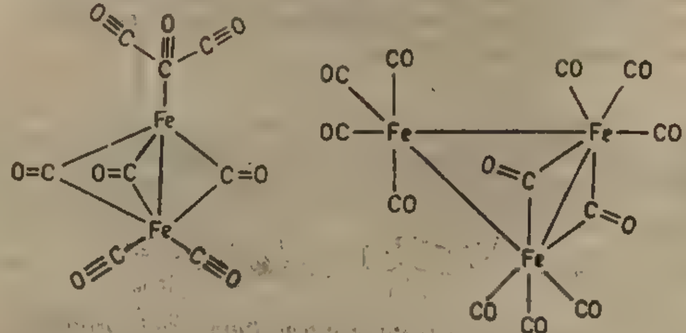
The transition metals form another class of orgamometallic compounds with carbon monoxide, called **metal carbonyls**. These compounds possess both σ- and π- bonding.

Some typical metal carbonyls are illustrated in Fig. 12.8.



Hexacarbonyl of Cr,Mo, or W (M=Cr,Mo or W) — Pentacarbonyl iron (o) — Tetracarbonyl nickel (o)

$M(CO)_6$ — $Fe(CO)_5$ — $Ni(CO)_4$



$Fe_2(CO)_9$ — $Fe_3(CO)_{12}$.

Fig. 12.8. Structures of some transition metal carbonyls.

12.8.1. Bonding in Organometallic Compounds

Bonding in metal carbonyls involve σ- and π-characters. The donor power of some ligands (*e.g.* CO) is insufficient for producing stable metal to ligand σ bonding. In such cases, the metal itself behaves as a donor to the ligand (π-bond is constituted). Thus, there is a mutual donation and acceptance of electrons on the part of both the metal and the ligand. In the case of carbonyls, the σ bonding arises from the overlap of the 2*p* orbital of the carbon with an empty orbital of the metal [Fig. 12·9 (*a*)]. The back co-ordination involves the overlapping of a metal d orbital (of π symmetry) containing electrons, with an empty antibonding π**p* orbital of CO [Fig. 12·9 (*b*)]. This results in the formation of a π M → C bond. According to MO theory, carbon monoxide has the electronic configuration

$$\sigma 1s^2,\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi\ 2p_x^2\ \pi\ 2p_y^2$$

and for every bonding π orbital there is a corresponding antibonding π-orbital. The π^*2p_x π^*2p_y orbitals are empty, and it is with

either of these that the d orbitals of the metal overlap [Fig. 12 9 (*b*)].

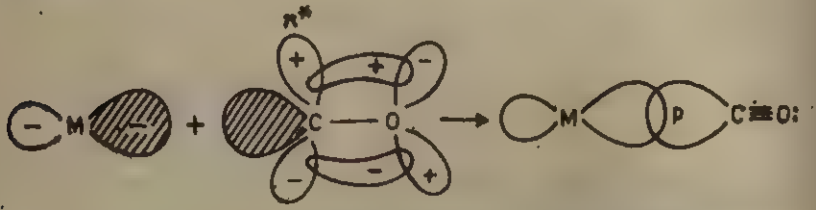


Fig. 12.9. (a) σ bonding system in a metal carbonyl. Donation of a lone pair of electrons in a p *orbital on carbon into a empty metal orbital. π orbital on CO is only shown in plane of the paper.*

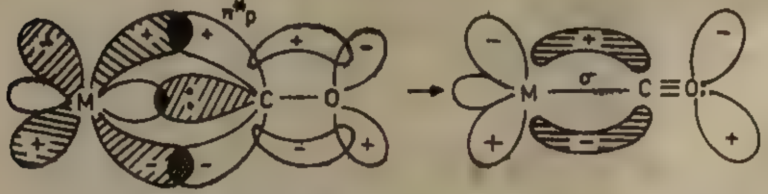


Fig. 12.9. (b) Back bonding in a transition metal carbonyl. Overlapping of a d *orbital of a metal (M) with an empty antibonding $\pi_p{}^*$ orbital of CO.*

The σ- and π bonding system can be portrayed as giver. Fig. 12.9 (*c*).

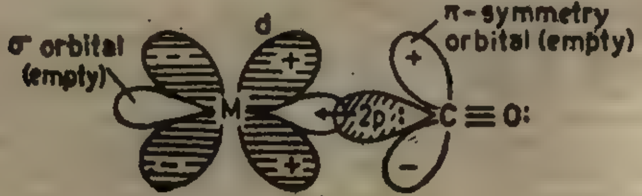


Fig. 12.9. (c) σ and π bondings system in a transition metal corbonyl.

In 1953, Chatt and Duncanson suggested that the bonding in a compound of an unsaturated hydrocarbon and a transition metal involves the coordination of the two π-electrons of the alkene double bond. In the case of alkene, the π electrons themselves are involved in σ bonding [Fig. 12.10 (*a*)] whereas the carbon of CO uses its lone pair of electrons to form σ bond.

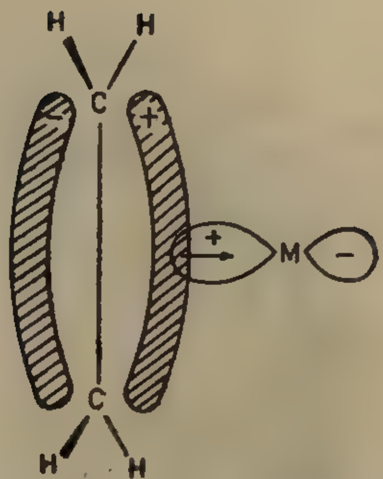


Fig. 12.10. (a) Bonding in metal-alkene complex. σ-donation from filled π-orbital of alkene into empty metal hybrid orbital.

The π electrons are thus shared between at least three atoms, and the bond would be quite weak without back donation from the transition metal d orbital to the π* antibonding orbital of alkene. Hence, it was proposed that the strength of the bond is reinforced by back donation of nonbonding d electrons of the metal atom to the empty π* orbitals of the alkene molecule [Fig. 12·10 (*b*)].

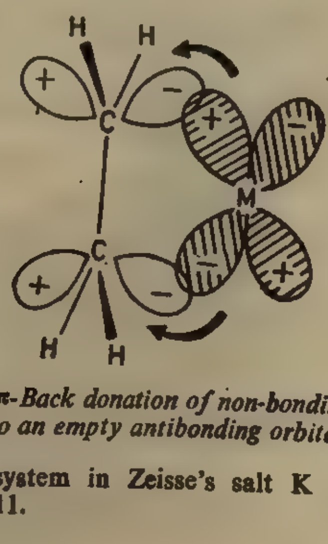


Fig. 12.10. (b) π-Back donation of non-bonding d *electrons to the metal into an empty antibonding orbital of alkene.*

The bonding system in Zeisse's salt K [Pt (C_2H_4) Cl_3] is illustrated in Fig. 12.11.

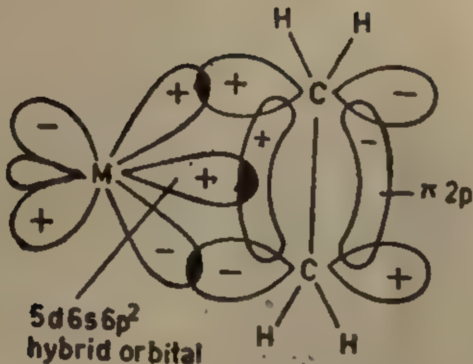


Fig. 12.11. The bonding in $[Pt(C_2H_4)Cl_3]^-$ ion

E.O. Fischer proposed that the bonding in ferrocene involves the donation ot three pairs of electrons from each $C_5H_5^-$ ring to the iron (II) ion. However, this model could not explain the aromatic substitution reactions of ferrocene because of the involvement of 6 electrons in the bonding to the metal.

Duntez and Orgel suggested that iron is joined by two covalent bonds to the two C_5H_5 rings (Fig. 12.12).

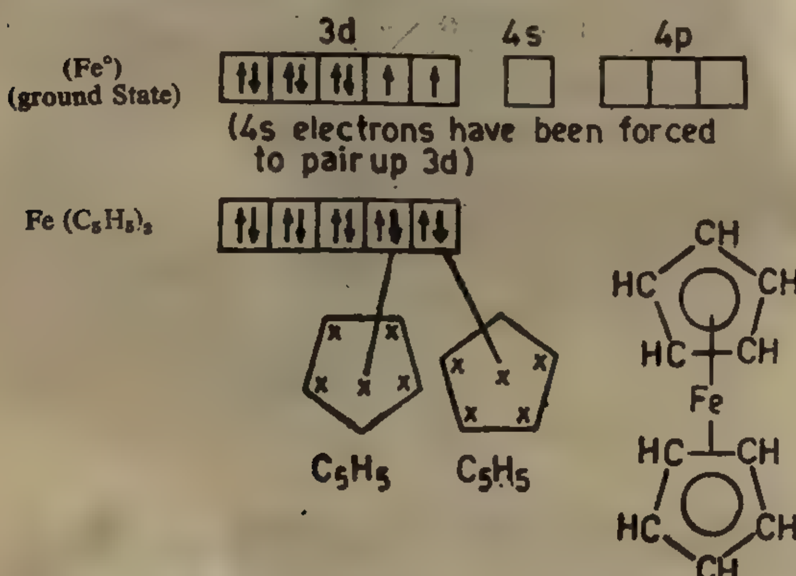


Fig. 12.12. Bonding system in ferrocene

12.8.2. Preparation of Organometallic Compounds

There are several methods of forming metal-carbon bonds. Some of the important methods are given below :

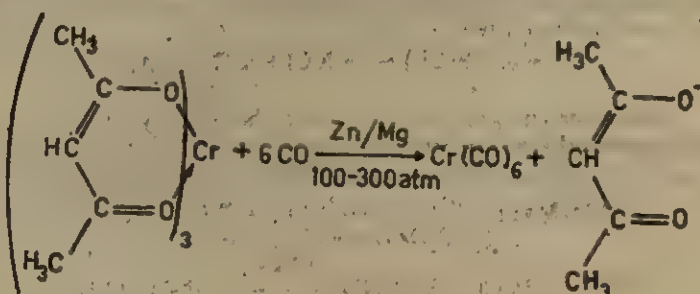
1. **Metal carbonyls** were prepared by direction carbonylation of the metal, reductive carbonylation, or thermolysis (also photolysis).

(*i*) Iron pentacarbonyl, $Fe(CO)_5$ and nickel tetra carbonyl, $Ni\,(CO)_4$ were prepared by Mond in 1890 by **direct reaction** between CO gas and the finely divided metal.

$$Ni + 4\,CO \xrightarrow[\text{atm pressure}]{330-350\text{ K}} [Ni\,(CO)_4]$$

Tetracarbonyl nickel (0)

(*ii*) **Reduction of compounds** of the metal in a solvent under high CO pressure is carried out. At times a neutral complex is used.



(in pyridine)

Grignard reagent can also be used as a reducing agent.

$$OsO_4 + 9\,CO \xrightarrow[\text{350 atm}]{\text{[redacted]}} Os(CO)_5 + 4\,CO_2$$

(*iii*) **Polynuclear carbonyls** are often as intermediates in the decomposition of the mono nuclear compounds. For example

$$6\,Fe\,(CO)_5 \xrightarrow[\text{(Photolysis)}]{h\nu} 3\,Fe_2\,(CO)_9 + 3\,CO$$
$$\downarrow 335\text{ K}$$
$$Fe_3\,(CO)_{12} + 3\,Fe\,(CO)_5$$

2. Organoalkali metal compounds and Grignard reagents are obtained by oxidative addition of an organic halide (RX) to a metal (Li, Na, K, Mg, Ca, Zn and Cd).

$$\underset{\text{(X-Cl, Br, I)}}{Mg + CH_3X} \xrightarrow{\text{[redacted]}} \underset{\text{(Grignard reagent)}}{CH_3Mg\,X}$$

$$2\,Li + C_6H_5\,Br \xrightarrow{\text{Ether}} LiBr + \underset{\text{Pheyl lithium}}{C_6H_5\,Li}$$

3. Group 14 metals tend to yield complex mixtures, such as RMX_3, RMX_2, R_3MX and R_4M. To obtain fully substituted derivative, R_4M, a large excess of Grignard reagent is required. Mixed alkyl metal halides can sometimes be isolated.

$$2\,PLLi + SnCl_4 \xrightarrow{\text{Ether}} \underset{\text{Dichloro diphenyl tin}}{Ph_2SnCl_2} + 2\,LiCl$$

$$PbCl_4 + 4\,C_2H_5MgBr \xrightarrow{\text{Ether}} 4\,MgBrCl + \underset{\text{Tetra ethyl lead}}{(C_2H_5)_4\,Pb}$$

$$SnCl_4 + 4\,BuLi \xrightarrow{\text{Ether}} 4\,LiCl + \underset{\text{Tetrabutyl tin}}{Bul_4Sn}$$

4. Among the π-complexes Zerisse's salt was the first to be isolated. It was prepared by the direct reaction between potassium tetra chloroplatinate (II) and ethylene in aqueous solution, followed by extraction with ether.

$$C_2H_4 + K_2\,[PtCl_4] \longrightarrow KCl + \underset{\text{Zeisse's salt}}{K\,[Pt\,(C_2H_4)Cl_3]}$$

Ferrocene is prepared as given below, by using C_5H_5Tl, C_5H_5MgBr and a strong organic base as proton acceptor.

$$FeCl_2 + 2\,TlC_5H_5 \longrightarrow 2\,TlCl + (\eta^5-C_5H_5)_2\,Fe$$

$$2\,C_5H_5MgBr + FeCl_2 \xrightarrow[\text{(Fe (III) is reduced to Fe (II))}]{} 2\,MgBrCl + (\eta^5-C_5H_5)_2\,Fe$$

$$2\,C_5H_6 + FeCl_2 + 2\,Et\,NH \xrightarrow[\text{amine}]{\text{in excess}} (\eta^5-C_5H_5)_2\,Fe + 2\,Et_2NH_2Cl$$

A series of chromium compounds was prepared by Hein by the reaction of $CrCl_3$ with C_6H_5MgBr. They were formulated as polyphenyl chromium compounds $(C_6H_5)_nCr$ where $n=2$, 3, or 4. The neutral compound dibenzene chromium, $(C_6H_6)_2$ Cr has also been prepared from the Grignard reaction of C_2Cl_3. It has also been prepared by heating anhydrous $CrCl_3$, $AlCl_3$, aluminium metal and benzene in an autoclave at 455 K.

$$3\,CrCl_3 + 2\,Al + AlCl_3 + 6\,C_6H_6 \rightarrow 3\,[Cr\,(C_6H_6)_2]^+ AlCl_4^-$$

Reduction with sodium dithionite gave $(\eta^6-C_6H_6)_2$ Cr as a brown-black solid.

13·8·3. Applications of Organometallic Compounds

Grignard reagent has been used extensively in organic chemistry for synthesizing various compounds (Units 7 and 8).

Organoalkali metal compounds are also used for synthetic purposes, *e.g.*, diphenyl is obtained by reaction of phenyl lithium with fluorobenzene.

$$C_6H_5F + C_6H_5\,Li \xrightarrow{H_2O} Li\,F + \underset{\text{Diphenyl}}{C_6H_5 - C_6H_5}$$

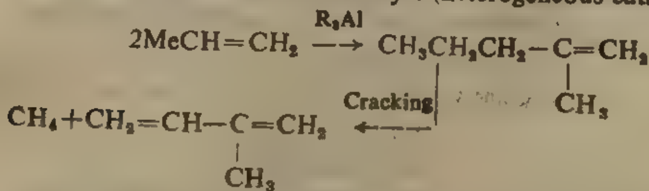
Manyl dialkyl zinc derivatives are commercially available and have been found useful in many syntheses.

$$2Zn\,Et_2 + 2H_2O \longrightarrow 2Zn\,(OH)\,Et + 2C_2H_6$$

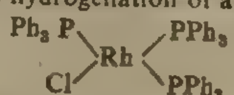
Dialkyl cadmium has been used for ketone synthesis.

$$R_2Cd + R'COCl \longrightarrow R'COR + CdCl_2$$

A major industrial process for making isoprene involves the use of a trialkyl aluminium catalyst (heterogeneous catalyst).



Some other organometallic compounds known as Wilkinson's and Nata catalysts are used for synthetic reactions. Wilkinson's catalyst is used in the hydrogenation of alkenes.



Tris (triphenyl phosphine) chlororhodium (I)
Wilkinson's catalyst (homogeneous catalyst)

Natta catalysts, the heteregoneous catalysts, are used in the polymerization of olefins. They are composed of a transition metal salt (usually $TiCl_3$) and a metal alkyl like triethylaluminium.

Pure nickel is obtained by contacting $Ni\,(CO)_4$ vapour with impure nickel pellets at 450 K, the compound being thermally unstable at this temperature.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

12.1. Choose the correct answer of the four alternatives given for the following :

(*i*) The number of unpaired electrons in tetrahedral $Ni\,(CO)_4$ complex is
(*a*) 0 (*b*) 2 (*c*) 3 (*d*) 4

(*ii*) Which of the following transition metal ions forms coloured complex ions ?
(*a*) Zn^{2+} (*b*) Ti^{4+} (*c*) Cu^{+} (*d*) Co^{2+}

(*iii*) What is the oxidation state of iron in $K_4\,[Fe\,(CN)_6]$?
(*a*) +3 (*b*) +2 (*c*) −3 (*d*) +4

(*iv*) Which one of the following is the most likely structure for the compound when 1/3 of the total chlorine in a compound with the empirical formula $CrCl_3 \cdot 6H_2O$ is precipitated with $AgNO_3$.

(*a*) $CrCl_3 . 6H_2O$
(*b*) $[CrCl_3 (H_2O)_3]\ 3H_2O$
(*c*) $[CrCl_2 (H_2O)_4]^+\ Cl^-,\ 2H_2O$
(*d*) $[CrCl (H_2O)_5]^{2+}\ (Cl^-)_2 . H_2O$.

(*v*) In which of the following compounds, the oxidation state of the nickel atom is zero.
(*a*) $KNiCl_3$ (*b*) $[Ni (NH_3)_6]\ Cl_2$
(*c*) $Ni (PF_3)_4$ (*d*) $Ni (CO)_4$

(*vi*) Which of the following systems has maximum number of unpaired electrons ?
(*a*) d^4 (octahedral) (*b*) d^9 (octahedral)
(*c*) d^7 (octahedral) (*d*) d^6 (tetrahedral).

(*vii*) Which of the following ligands produces strong field ?
(*a*) H_2O (*b*) NH_3
(*c*) CN^- (*d*) none.

(*viii*) What is the coordination number of chromium in $[Cr (NH_3)_3 (H_2O)_3]\ Cl_3$?
(*a*) 3 (*b*) 4 (*c*) 5 (*d*) 6

(*ix*) Which of the following complex species does not involve d^2sp^3 hybridization ?
(*a*) $[CoF_6]^{3-}$ (*b*) $[Co (NH_3)_6]^{3+}$
(*c*) $[Fe (CN)_6]^{3-}$ (*d*) $[Cr (NH_3)_6]^{3+}$.

(*x*) The two complexes $[Co (NH_3)_5\ Br]\ SO_4$ and $[Co (NH_3)_5\ SO_4]\ Br$ represents
(*a*) linkage isomerism (*b*) ionization isomerism
(*c*) optical isomerism (*d*) coordination isomerism.

12.2. Fill in the blanks with appropriate words.

(*i*) Coordination compounds have increased stability when they involve ......ligands.
(*ii*) The valence bond model does not provide explanation for the......
(*iii*) Crystal field theory permits an explanation of both the......of complexes.
(*iv*) The spliting of the d orbital energy levels depends upon the......
(*v*) The $[Pt (NH_3)_4]^{2+}$ ion is diamagnetic. Its geometry is......
(*vi*) The ion with $(CoCl_4)^{2-}$ tetrahedral geometry has......unpaired electrons.
(*vii*) Linkage isomer of $[Co (-NO_2) (NH_3)_5]\ Cl_2$ is......
(*viii*) The bonding between the metal and the cyclopentadienyl ring involves overlapping of ......orbitals of the ring with empty...... orbitals of the metal.
(*ix*) The bonding in $[Pt\ Cl_3 (C_2H_4)]^-$ is envisaged in terms of ligand to metal donation by the overlapping of one of the ethylene π bonding lobes with an empty......orbital of platinum (II), supplemented by a......form the platinum to......of the ethylene.
(*x*) Stereoisomerism arises when the formula of a complex ion or neutral molecule corresponds to more than one......of the ligands in the...... sphere.

12.3. Which of the following statements are true (T) and false (F) :

(*i*) Colour is the same in different complexes of a metal in the same oxidation state.

(*ii*) Metals other than iron do not form sandwich compound like $Fe(C_5H_5)_2$.

(*iii*) cis-Diamminedichloroplatinum (II), $[Pt(NH_3)_2Cl_2]$ is a neutral molecule

(*iv*) Cis and trans isomers possess different physical and chemical properties and they are termed geometrical isomers.

(*v*) Ionization isomerism occurs when it is possible for anionic ligands to interchange with anions outside the coordination sphere.

(*vi*) The stability of complexes depends upon the nature of the metal only.

(*vii*) The bis(dimethylglyoximato) nickel (II) assumes octahedral geometry.

(*viii*) $[Ni(CN)_4]^{2-}$ ion is paramagnetic in nature.

(*ix*) In all the carbonyls, carbonyl group behaves as ketonic group.

(*x*) The complex $[Co(NH_3)_6][Cr(C_2O_4)_3]$ is given the name hexaammine cobalt (III) trioxalatochromium (III).

SHORT ANSWER QUESTIONS

12.4. How would you distinguish between the isomer pairs ?

(*a*) (1) $[Co Br(NH_3)_5]SO_4$ and (2) $[Co(SO_4)(NH_3)_5]Br$

(*b*) (1) $[Cr(H_2O)_6]Cl_3$ and (2) $[Cr(H_2O)_5Cl]Cl_2 . H_2O$

(*c*) (1) cis $[Pt Cl_2(NH_3)_2]$ and (2) trans $[Pt Cl_2(NH_3)_2]$

(*d*) The two enantiomers of $[Co Cl_2(en)_2]^+$.

12.5. Name the following coordination compounds using IUPAC norms :

(*a*) $[Cr(NH_3)_6]^{3+}$ (*b*) $[Ni(NH_3)_6]Cl_2$

(*c*) $[Mn(H_2O)_6]^{2+}$ (*d*) $[Co(en)_3]^{3+}Cl_3$

(*e*) $[Fe(CN)_6]^{4-}$ (*f*) $Na[CoCl_4(NH_3)_2]$

(*g*) $[Cr(NH_3)_4Cl(H_2O)]Cl_2$ (*h*) $[Cr F_2(en)_2]Cl$

12.6. Write down the formulae of the following coordination compounds :

(*a*) hexaammineplatinum (IV) chloride

(*b*) potassiumhexacyanoferrate (III)

(*c*) diamminedichloroplatinum (II)

(*d*) tetraamminedichlorocobalt (III) ion

(*e*) amminechlorobis (ethylenediamine) cobalt (III) ion

(*f*) Triammine trichloro cobalt (III)

(*g*) Potassium diaquabis(oxalato) chromate (III)

(*h*) tetrathiocyanatocobaltate (II) ion.

12.7. Arrange the following complexes in order of increasing electrical conductivity.

$[Co Cl_3(NH_3)_3]$, $[Co Cl(NH_3)_5]Cl_2$, $[Co(NH_3)_6]Cl_3$ and $[Co Cl(NH_3)_5]Cl$

12.8. How many d electrons does the metal have in each complex species ?

(*a*) $[Zn Cl_4]^{2-}$ (*b*) $[Cr Cl_6]^{3-}$

(*c*) $[Ni(NH_3)_6]^{2+}$ (*d*) $[Co C_2O_4(en)_2]^+$.

TERMINAL QUESTIONS

12.1. How will you distinguish between the following pairs :

(*i*) double salt and complex salt

(*ii*) paramagnetic and diamagnetic compounds

(*iii*) ionic and neutral coordination compounds

(*iv*) ionization isomers and coordination isomers
(*v*) coordination number and oxidation number.

12.2. Define and explain the following terms :
(*a*) ligand (*b*) chelate
(*c*) coordination number (*d*) coordination sphere.

12.3. Enumerate the salient features of Werner's coordination theory.

12.4. What is meant by unidentate, bidentate, and polydentate ligands. Give two examples for each. It is true that a cyclic complex is usually more stable than an open one. Substantiate your answer with an example.

12.5. Give any two methods which are employed in the preparation of coordination compounds. Give their important properties.

12.6. What geometries are possible for a coordination complex with emiprical formula $Pt\ Cl_2 . 4NH_3$? What will be structure if the complex is assumed to be diamagnetic ?

12.7. Name the various types of isomerism shown by coordination compounds. Give one example of each type.

12.8. Draw all the possible isomers (structural and stereoisomeric) having the composition $CrBr_2Cl\ (NH_3)_4$.

12.9. Draw the structure of each complex species on the basis of VBT.
(*a*) $[Fe\ F_6]^{3-}$ (*b*) $[Zn\ Cl_4]^{2-}$
(*c*) $[Cu\ Cl\ (H_2O)_3]^{+}$ (*d*) $[Fe\ (CN)_6]^{3-}$.

12.10. (*i*) Draw the possible optical isomers of each of the following :
(*a*) $[Cr\ Cl_2\ (en)_2]^{+}$ (*b*) $[CoCl_2\ (NH_3)_2\ en]^{+}$
(*ii*) Draw the possible geometrical isomers of each complex :
(*a*) $[Cr\ Cl_2\ (en)_2]^{+}$ (*b*) $[Co\ (NO_2)_3\ (NH_3)_3]$
(*c*) $[Fe\ (OH)_2\ (H_2O)_4]$ (*d*) $[Pt\ Cl_2\ en]$.

12.11. What is meant by stability of a coordination compound in solution. State the factors which govern the stability of complexes. In what ways the concept of stability of complexes has been helpful in analytical chemistry and tatrimetric analysis ?

12.12. Comment on the importance of coordination compounds.

13. What are organometallic cempounds ? What are the broad classes of these compounds ? Give one example of each type.

12.14. Explain the bonding involved in Zeisse's salt and metal carbonyl ? Give the representative structures.

12.15. Give a few methods used for the preparation of organometallic compounds.

ANSWERS TO SELF ASSESSMENT QUESTIONS

12.1. (*i*) (*a*) (*ii*) (*d*) (*iii*) (*b*) (*iv*) (*c*) (*v*) (*d*) (*vi*) (*d*)
(*vii*) (*c*) (*viii*) (*d*) (*iv*) (*a*) (*x*) (*b*).

12.2. (*i*) multidentate
(*ii*) colour variation in complexes
(*iii*) magnetic properties and colour
(*iv*) nature of the coordinated ligand
(*v*) square planar
(*vi*) three

(*vii*) $[Co(-ONO)(NH_3)_5]Cl_2$
(*viii*) π, d
(*ix*) dsp^2, back coordination, empty antibonding π^* orbital
(*x*) spatial arrangement, coordination.

12.3. (*i*) F (*ii*) F (*iii*) T (*iv*) T (*v*) T (*vi*) F
(*vii*) F (*viii*) F (*ix*) F (*x*) F.

12.4. (*i*) (*a*) Isomer (1) gives white ppt. of $BaSO_4$ on treating with $BaCl_2$. Isomer (2) forms no precipitate.
(*b*) The water molecule in isomer (2) is lost easily on heating. While the water molecules in isomer (1) are not lost easily being coordinated to the central atom.
(*c*) cis isomer (1) has dipole moment ; the trans isomer (2) does not.
(*d*) One enantiomer is dextrorotatory and the other is laevorotatory.

12.5. (*a*) Hexaammine chromium (III) ion
(*b*) Hexaammine nickel (II) chloride
(*c*) Hexaaquamanganese (II) ion
(*d*) Tris (ethylenediamine) cobalt (III) chloride
(*e*) Hexacyanoferrate (II) ion
(*f*) Sodium diammine tetrachloro cobaltate (III)
(*g*) Tetraammineaquachloro chromium (III) chloride
(*h*) Bis(ethylenediamine) difluoro chromium (III) chloride.

12.6. (*a*) $[Pt(NH_3)_6]Cl_4$ (*b*) $K_4[Fe(CN)_6]$
(*c*) $[Pt(NH_3)_2Cl_2]$ (*d*) $[Co(NH_3)_4Cl_2]^+$
(*e*) $[Co(en)_2NH_3Cl]^{2+}$ (*f*) $[CoCl_3(NH_3)_3]$
(*g*) $K[Cr(C_2O_4)_2(H_2O)_2]$ (*h*) $[Co(SCN)_4]^{2-}$.

12.7. $[CoCl_3(NH_3)_3] < [CoCl(NH_3)_5]Cl < [CoCl(NH_3)_5]Cl_2 < [Co(NH_3)_6]Cl_3$

12.8. (*a*) d^{10} (*b*) d^8 (*c*) d^8 (*d*) d^6

□ □

UNIT 13

Nuclear Chemistry

Vast new fields which have been opened by the advent of atomic energy are only just beginning to be explored.

UNIT PREVIEW

13.1. Introduction.
13.2. Radioactivity.
13.3. Nuclear structure and nuclear properties : stability of nucleus, binding energy, nuclear changes, group displacement law.
13.4. Radioactive disintegration series.
13.5. The kinetics of nuclear decay half-life period, units of radioactivity.
13.6. Nuclear reactions (transmutations) : artificial transmutation of elements artificial radioactivity.
13.7. Synthetic elements.
13.8. Nuclear fission ; atomic bomb, nuclear reactor, breeder reactors.
13.9. Nuclear fusion.
13.10. Applications of radioactivity and radioisotopes
Self assessment questions
Terminal questions
Answers to self assessment questions.

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Define and explain radioactivity.
2. Distinguish between ordinary chemical reactions and nuclear reactions.
3. Describe the three types of radiations—alpha particle, beta particle and gamma radiation.
4. Understand the meaning of the following terms :
   nucleon, nuclide, projectile, tar et, emission, positron, mass defect, electron capture.
5. List and write the symbols for the primary particles and radiation associated with nuclear changes.
6. Write balanced chemical equations for nuclear changes
7. Understand the significance of group displacement law.
8. Define half-life as it applies to the decay of radioactive elements.
9. Distinguish between natural and induced radioactivity.
10. Describe the factors related to nuclear stability and other nuclear properties.
11. Explain the nature of nuclear transformations through particle bombardment and the transformations used to prepare synthetic elements.

12. State the nature of the nuclear fission reaction, the source of the energy produced, and the methods used to control fission in nuclear reactors for power generation.
13. Describe the nature of the nuclear fusion reaction and the various problems encountered in such reactions.
14. Comment on the application of radioactivity and radionuclides.
15. Attempt various numerical exercises based an various cancepts explained in the unit.

13.1. INTRODUCTION

Atom is composed of a nucleus surrounded by extra nuclear electrons. The chemical properties of an element mainly depends upon the electrons. The nuvleus of an atom is a site of high concentration of mass and positive charge, and is composed of protons and neutfons (nucleons). The many other nuclear particles which have been found are involved primarily in binding energies between the fundamental particles—protons and neutrons. Nuclei of all atoms of the same element always contain the same number of protons, but may differ in their number of neutrons.

The nucleus, except for its charge which influences the electrons, takes no part in the chemical activity. In this unit, we shall turn our attention to atomic nuclei, an area of study called **nuclear chemistry**.

Atoms of most nuclides are stable, that is they do not undergo any change of their own accord. However, there are some nuclides, whose nuclei undergo changes of their own accord producing new nuclei, a process discovered in 1896 by Henri Becquerel. Several types of changes have been recognized, and the rate of change varies tremendously form one nucleus to another. During the changes, the unstable atomic nuclei limit radiations. The phenomenon of emitting radiations is said to be **radioactivity** and the unstable nuclides are said to be **radioactive**.

There are many nuclear transformations by which the nucleus of an element changes, into the nucleus of another element which are of relevance to chemistry. Examples of these nuclear reactions are **radioactive decay, artificial transmutation, nuclear fission** and **nuclear fusion.** These topics constitute the subject-matter of this unit.

With artificial transmutation it has been possible to synthesize transuranic elements. Nuclear fission and nuclear fusion reactions hold the promise of providing mankind with a vast source of energy thereby reducing our dependence on fossil fuels for our energy requirements. It has also been postulated that some hydrogen to helium nuclear reaction produces the sun's energy.

13·2. RADIOACTIVITY

The spontaneous breakdown of the nuclei of unstable atoms like radium through the emission of active radiation is called **natural radioactivity**. It is unaffected by external conditions such as temperature, pressure and chemical environment. This phenomenon was first identified in 1896 by Henry Becquerel.

During the course of research concerned with X-rays and fluorescence, Becquerel happened to store his research material-potassium uranyl sulphate, $K_2(UO_2)(SO_4)_2.2H_2O$ and photographic plate (wrapped in a black paper)—in one place but in close contact. Upon developing the plate later, he observed that the plate appeared to have been light struck (on the basis of dark spots on the plate). Later he interposed certain opague materials between photographic plate and uranium mineral. The same results recurred. Becquerel convinced himself that without the excitation of the sun light, the uranium mineral had been emitting some form of radiation that could penetrate materials normally opaque to light. This phenomenon was taken to be related to radioactivity.

Intrigued by Becquerel's discovery, Marie Curie (Becquerel's student) and her husband Pierre Curie started to investigate this new type of radiation. They demonstrated that the phenomenon was also characteristic of other substances. They succeeded in isolating, two new elements, polonium (named after Marie Curie's homelavel Poland) and radium (named after the Latin word for a ray) from the pitchblende, an ore of uranium. Both these elements were found to be radioactive more radiactive than uranium. Since then many elements that are radioactive have been recognized. Naturally occurring radioactive elements can also induce radioactivity in other

(This stamp is from Poland, the country of her birth)

Marie Sklodowska Curie (1867—1934)

substances. The phenomenon is called **induced** or **artificial radioactivity.**

13.2.1. Nature of Radiations

The radiations emitted from radioactive nuclides and their salts have been found to be composed of three types of radiations, alpha (α), beta (β) and gamma (γ) rays on the basis of the deflections experienced by the radiations in strong electric and magnetic fields (Figs. 13.1 and 13.2). These radiations can ionize gases and other substances. They are of high energy.

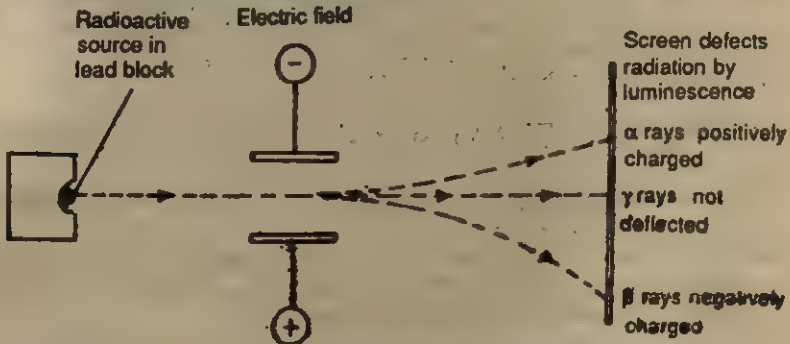


Fig. 13.1. Radiations from a rodioactive source are separated into α, β and γ radiations in an electrostatic field. The α rays are positively charged, the β rays are negatively charged and the γ rays are uncharged.

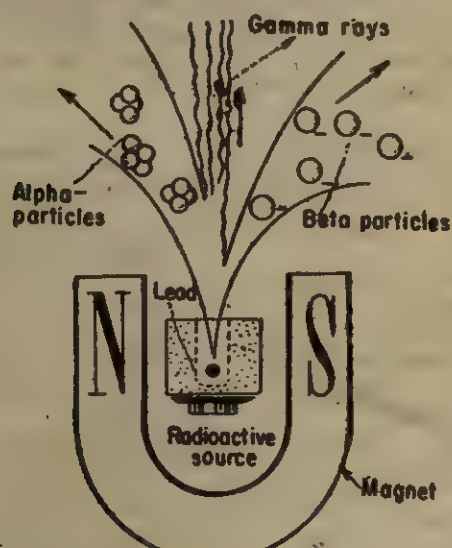


Fig. 13.2. Behaviour of α, β and γ rays in magnetic field

Alpha rays. These rays consist of particles. An α particle , the nucleus of a helium atom, with a relative mass of 4 and a charge of 2+. Thus, it is regarded as a dipositive helium ion, He^{2+}

(or helium nuclei denoted as $^{4}_{2}He$; also $^{4}_{2}\alpha$). The velocity of prticles

is very high, $1-2\times10^{4}$ to $3{\cdot}2\times10^{4}$ ms^{-1} ($\leqslant$10% of speed of light). Inspite of high velocity, they are not very penetrating because of their heavy mass (Fig. 13·3). They can be stopped by a sheet of paper, very thin aluminium foil (>0 02 cm) or a few centimetres of air, They experience small deflection in electric and magnetic fields due to their heavy mass and momentum.)

Beta rays. These rays consist of negatively charged particles

identical to electrons (denoted by $^{0}_{-1}e$ or $^{0}_{-1}\beta$). They move with a velocity

of $9{\cdot}6\times10^{7}$ to 25×10^{7} ms^{-1} ($\leqslant$90% of speed of light). Their pentrating power is about 100 times more than α-rays. They can- stopped by thin sheets of metal (>0·2 cm).

Gamma rays. Gamma rays are a form of electromagnetic radiations comparable with X-rays but of shorter wavelength (~ 10 ·)

Because of their short wavelenth, γ rays possess more energy th n X-rays. They travel at the velocity of light. These rays have a greater range than α and β radiation and are able to penetrate considerable thickness of materials (~100 cm thick aluminium sheet)

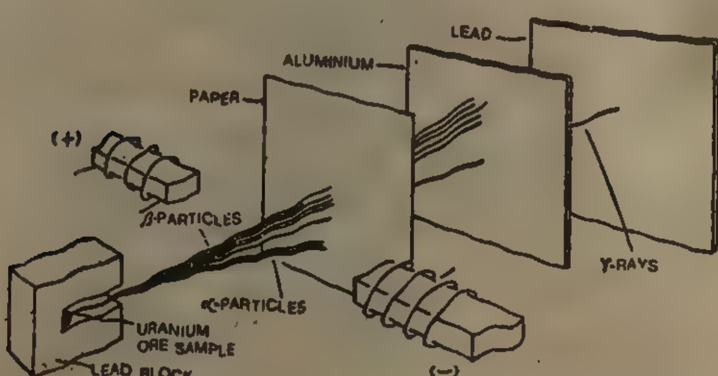


Fig. 13.3. Relative penetrating power of α, β and γ rays

even those of high density. They are not deflected in electric and magnetic fields.

Some less common forms of radioactive emissions include **neutrons, protons, positrons** (particles bearing a positive charge but having the same mass as an electron) and **deuterons** (particles containing a proton and a neutron).

13.3. NUCLEAR STRUCTURE AND NUCLEAR PROPERTIES

Rutherford discovered in 1909 that atoms have very small nuclei (radius of 10^{-13} cm), which contain almost all the atomic mass. The nuclei of atoms are, therefore, extremely dense. Protons and neutrons often called **nucleons** are the major particles that constitute the nucleus. In addition to protons and neutrons, many very short lived subatomic particles have been detected as products of nuclear reactions. There is evidence that protons and neutrons themselves have internal structures. Away form the nucleus, the neutron decays into a proton and an electron.

$$n \longrightarrow p + e^- + \underset{\text{(antineutrino)}}{\bar{\nu}}$$

Table 13.1 includes some of the important particles.

TABLE 13.1. A few subatomic particles of nucleus

Particle	*Symbol*	*Mass*	*Charge*
Antiproton	$_{-1}^{1}H$	same as that of proton	negative
Neutrino	ν	extremely lighter than electron	zero
Positron	$_{1}^{0}e$ (or β^+)	same as that of an electron	positive
(μ-meson (muon)		~210 times that of an electron	positive and negative
π-meason (pion)		276 times that of an electron 265 times that of an electron	positive and negative zero

The nucleus is unique in the sense that it is a minute fraction of the total volume of an atom and contains a very high concentration of positive charge. Clearly, to overcome such electrostatic repulsion and produce such condensed mass, exceptional attractive forces must be present.

Any nuclear species characterized by its atomic number and mass number (total number of protons and neutrons) is called **nuclide** and is denoted by the symbol, $^{\text{mass number}}_{\text{atomic number}}E$, where E is the element (*e.g.*, $^{12}_{6}C$, $^{1}_{1}H$, $^{16}_{8}O$, $^{35}_{17}Cl$).

Two nuclides with same atomic number but different mass number are said to be isotopes, *e.g.* $^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$.

13.3.1. Stability of the Nucleus

It is a natural phenomenon that every matter tries to attain stability. In the process of attainings stability certain nuclei undergo rodioactive decay.

It is thought that, in some way, the strong force of mutual repulsion between the protons within the nucleus is overcome by the presence of neutrons, which thus help to stabilize the nucleus. It has been seen that for a stable nucleus the ratio of the number of protons to the number of neutrons lies between certain limits, as shown in Fig. 13.4. Nuclides whose ratios of neutrons to protons lie in the shaded region (belt of stability) are stable. Nuclides that lie outside the belt of stability are unstable and decay in a manner that tends to given them a stable neutron to proton' (n/p) ratio. Above the shaded region, the nucleus contains exccess neutrons and is radioactive. Such a nucleus either lose neutrons or gain protons

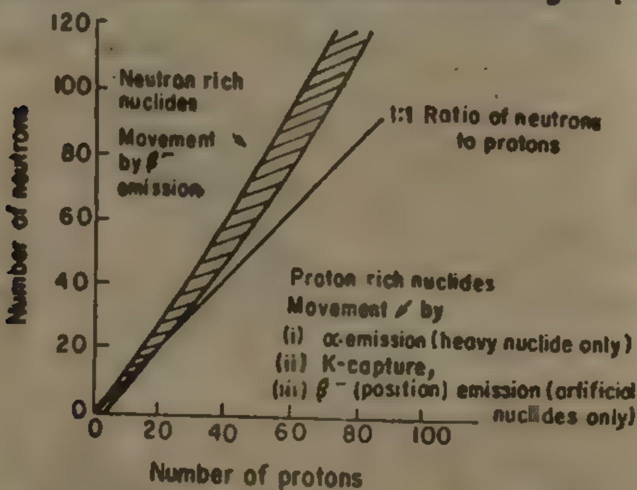


Fig. 13.4. Nuclear stability curve neutron-proton ratio

to achieve stability. The nucleus of ${}^{14}_{6}C$ decays by β-emission (this process converts a neutron into a proton).

$$ {}^{1}_{0}n \longrightarrow {}^{1}_{1}p + {}^{0}_{-1}e $$

$$ {}^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e $$

Elements located below the belt of stability must increase their (n/p) ratio to achieve stability. This is accomplished in either of two ways.

(*i*) **by the emission of positron (${}^{0}_{1}e$) :**

In the emission of a positron, a proton in the nucleus is converted into a neutron

$$ {}^{1}_{1}p \longrightarrow {}^{1}_{0}n + {}^{0}_{1}e $$

i.e.,

$$ {}^{11}_{6}C \longrightarrow {}^{11}_{5}B + {}^{0}_{1}e $$

(*ii*) **by electron capture (*K*-capture) :**

As the captured electron generally, originates in the *K* shell, the process is also called *K*-capture. As a result of addition of electron to the nucleus, a proton converts into a neutron.

$$ {}^{1}_{1}p + {}^{0}_{-1}e \longrightarrow {}^{1}_{0}n $$

(Electron capture)

i.e.

$$ {}^{7}_{4}Be + {}^{0}_{-1}e \xrightarrow{K\text{-capture}} {}^{7}_{3}Li $$

$$ {}^{40}_{19}K + {}^{0}_{-1}e \xrightarrow{K\text{. capture}} {}^{40}_{18}Ar $$

At higher atomic numbers the (n/p) ratio reaches beyond 1·5 for the largest stable nucleus, ${}^{209}_{83}Bi$. All elements having atomic numbers higher than 83, *i.e.*, those beyond the end of the stability belt appear to be too large to be stable, and a reduction in the overall size of the nucleus is effected by the loss of an α-particle.

$$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He$$

From the above discussion we conclude that unstable nuclei lie either above, below or beyond the end of the belt of stability. Such nuclei tend to undergo transformation into nuclei lying within the belt or, at least, closer to it. Unstable nuclide tries to attain stability by spontaneous emission of α or β particles. These are simultaneously accompanied by γ radiations.

Sometime a nucleus which is far beyond the end of the belt of stability splits into several much lighter fragments. This process, **nuclear fission**, is one of the modes by which uraminum. 235 can spantaneously decay.

$$^{235}_{92}U \longrightarrow {}^{140}_{56}Ba + {}^{92}_{36}K + 3\,{}^{1}_{0}n$$

Fragments produced on fission, if unstable, undergo simpler types of decay producing a stable nucleus. We shall discuss about the nuclear fission in a later section.

Binding energy

The stability of a nucleus is measured by its binding energy. The energy released when the nuclear particles coalesce forming a nucleus. A nucleus with high binding energy (per nucleon) is more stable than one in which the binding energy is low. This energy is the consequence of mass lost experienced on combining of the component nucleons (an exothermic process).

An analysis of the number of protons and neutrons in the stable nuclides reveals that nuclei such as

$^{4}_{2}He$, $^{8}_{4}Be$ $^{12}_{6}C$, $^{16}_{8}O$, $^{20}_{10}Ne$ and $^{24}_{12}Mg$ are more stable. All these nuclei contain an even number of protons and neutrons. Thus it is established that nuclei containing even numbers of neutrons and protons are more stable than the other nuclei. This is evident from the binding energies per nucleon or by the large number of stable nuclei in which the even number of both protons and neutrons occur (Fig. 13.5), This is because the two nucleons (have spin and act as tiny magnet) pair up so as to cancel out their spins. Only five nuclides

$^{2}_{1}H$, $^{6}_{3}Li$, $^{10}_{5}B$, $^{14}_{7}N$ and $^{180}_{73}Ta$ have an odd number of both protons and neutrons.

13.3.2. Nuclear Structure

The neutron/proton ratio, nuclear size and binding energy help in understanding the nuclear structure. Stable nuclei of the lighter

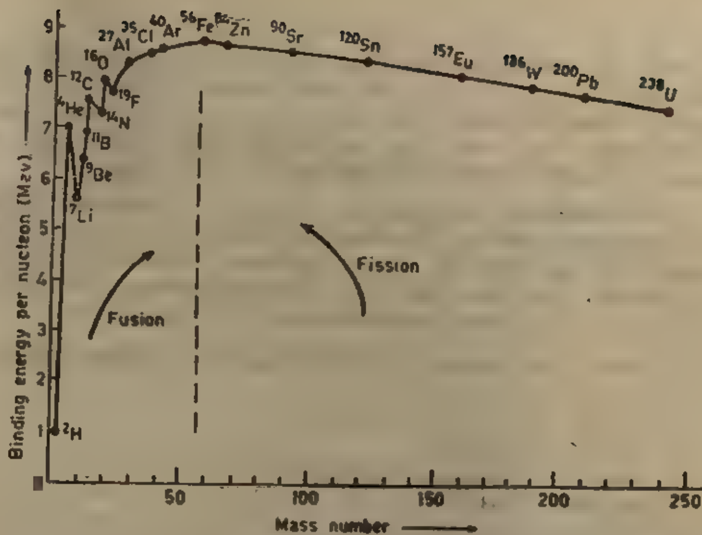


Fig. 13.5. Relative stability curve for nuclei.

elements have neutron to proton ratios of about 1 : 1, but for the heavier elements to be stable there must be more neutrons than protons to keep a nucleus from flying apart as a result of proton-proton repulsion. The small size of the nucleus puts the limit to the number of protons that can be packed into such a small volume. It further suggests that the attractive forces holding it together must operate at very close range and therefore only between immediate neighbours.

A theory of cohesive forces between nucleons was proposed by Hidekei Yukawa in 1935. Yukawa explained the stability of nucleus containing many protons and neutrons by suggesting that π-mesons (particles) provide the nuclear glue.

These particles are continuously exchanged between neutrons and protons to produce strong exchange forces which bind these particles together. These π-mesons (from the Greak mesos 'intermediate' may be π^+, π^-, or π°. Its mass is ~275 times that of a electron. A neutron on losing a π^- becomes a proton ; the π^- is taken on by a second proton to form a new neutron.

$$n_1 \longrightarrow p_1^+ + \pi^-$$
$$p_2^+ + \pi^- \longrightarrow n_2$$

In a similar way, π^+ mesons are rapidly exchanged between protons and neutrons and π° mesons between two protons and between two neutrons.

13.3.3. Nuclear Changes (Modes of Radioactive Decay)

The radioactive decay results into nuclear changes ; new nuclei along with radiations are obtained. A nucleus can decay by α, β and

γ emission. There may be more than one type of emission, although a particular nucleus cannot emit both α and β particles simultaneously. A few radioactive nucleides, *e.g*, Bi-214 (uranium series) and K-40 (can decay into both As-40 and Ca-40) decay partly by one mode while others change by another, but this is rare.

(*i*) **α-Emission.** Because an α particle is composed of two protons and two neutrons, its emission results into a new nucleus (daughter nucleus) with an atomic number 2 units less and mass number 4 units less than the parent nucleus (decaying element) in the periodic table. Heavier nuclei undergo this type of decay.

The decay can be represented by the general nuclear equation :

$$\underset{\text{Parent nucleus}}{{}^{M}_{Z}X} \longrightarrow \underset{\text{Daughter nucleus}}{{}^{M-4}_{Z-2}X} + \underset{\alpha\ \text{Particle}}{{}^{4}_{2}He}$$

Some illustrations of α-decay are :

$${}^{238}_{92}U \longrightarrow {}^{234}_{90}Th \longrightarrow {}^{4}_{2}He$$

$${}^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

Any decrease in mass during α particles emission, howsoever small, will be converted into energy in the form of γ-rays. The daughter nucleus is expected to be formed as negative ions as a result of emission of positively charged α particles. In fact it is neutral, because two extranuclear electrons are lost at the same time as the α particles. These two electrons do not orginate from the nucleus hence are not regarded as β particles.

(*ii*) **β-Emission.** The loss of a β-particle from an atomic nucleus causes an increase of 1 unit in the atomic number, but no change in the mass number of the nucleus. The decay occurs through the conversion, in the nucleus, of a neutron into a proton and an electron :

$$n \longrightarrow p^{+} + e^{-}$$

The proton is left behind in the nucleus, which raises its atomic number by one unit. The electron, however, leaves the nucleus as a β particle. Neutrino (ν) is emitted to conserve energy.

$$\underset{\text{Parent nucleus}}{{}^{M}_{Z}X} \longrightarrow \underset{\text{Daughter nucleus}}{{}^{M}_{Z+1}X} + \underset{\beta\ \text{particle}}{{}^{0}_{-1}e} + \underset{\text{Neutrino}}{\nu}$$

Some illustrations of β-decay are :

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

$$^{234}_{90}Th \longrightarrow {}^{234}_{91}Pa + {}^{0}_{-1}e$$

$$^{214}_{82}Pb \longrightarrow {}^{214}_{83}Bi + {}^{0}_{-1}e$$

Thus, as a result of β-emission, the daughter nucleus formed is one place to the right of the parent nucleus in the periodic table. The mass number of the new nuclide, however, continues to be the same as that of the decaying nuclide, because the sum of the protons and neutrons is unaltered. As with α-emission, the new nuclide is electrically neutral, because the extra proton in the nucleus is balanced by the acceptance of a stray electron into the shells of the atom.

The changes brought about by the emission of an α or β particle from the nucleus are described by the **group displacement law.**

(*iii*) **γ-Emission.** Emission of γ-radiation can have several causes :

(*a*) The emission of either α or β particles may be accompanied by γ-radiations. The loss of γ-rays does not change the atomic number or the mass number of an atom. In a certain nuclear transformation the daughter nucleus is formed in an excited state. When this nucleus drops from the excited state to a lower energy state (ground state) γ-rays are emitted.

$$^{119}_{50}Sn \xrightarrow{\text{Internal transition}} {}^{119}_{50}Sn + \gamma$$

$$^{222}_{86}Rn \xrightarrow{\text{Internal transition}} {}^{222}_{86}Rn + \gamma$$

(*b*) At times electron capture also accompanies γ-radiation. Generally the electron from the *K*-shell is captured by a proton and the vacancy of electron in the *K*-shell is filled by an electron from a higher shell. In the process, proton is converted into a neutron and the mass number of the parent nucleus remains the same, but its atomic number decreases by one unit.

$$^{85}_{38}Sr + {}^{0}_{-1}e \longrightarrow {}^{85}_{37}Rb$$

(Electron capture)

γ-Emission then occurs from the excited nucleus as stated earlier.

(*c*) The emission of γ-radiation is, at times, also accompanied by the emission of positrons. Free positrons, on emission, combine with a stray electron to give γ-radiation.

$$ {}^{30}_{15}\text{P} \longrightarrow {}^{30}_{14}\text{Si} + {}^{0}_{1}e $$

No naturally occurring nuclides decay in this way.

Group Displacement Law. It was originally formulated by Rutherford, Soddy and Fajans. This law describes the changes experienced by nuclides as a result of α-and β-emissions.

The following illustrations will explain the law clearly :

1. Loss of an α-particle from ${}^{218}_{84}\text{Po}$ produces radioactive lead

i.e., $\left[{}^{214}_{82}\text{Pb} \right]$.

$$ {}^{218}_{84}\text{Po} \longrightarrow {}^{214}_{82}\text{Pb} + {}^{4}_{2}\text{He} $$

This product is an isotope of an element which belongs to group 14, *i.e.*, two places to the left of the parent element (group 16 element).

2. Radioactive lead, ${}^{214}_{82}\text{Pb}$ loses a β particle. The daughter element thus produced is called radioactive bismuth, ${}^{214}_{83}\text{Bi}$.

$$ {}^{214}_{82}\text{Pb} \longrightarrow {}^{214}_{83}\text{Bi} + {}^{0}_{-1}\text{e} $$

This product is an isotope of an element which belongs to group 15, *i.e.*, one position to the right of the parent element (group 14 element). Thus, β-emission produces isobars.

3. Radioactive bismuth, ${}^{214}_{83}\text{Bi}$ decays to polonium ${}^{214}_{84}\text{Po}$ on losing a β particle.

$$ {}^{214}_{83}\text{Bi} \longrightarrow {}^{214}_{84}\text{Po} + {}^{0}_{-1}\text{e} $$

This product is an isotope of an element which belongs to group 16, *i.e.*, one position to the right of the parent element (group 15 element).

In brief, if a nucleus loses an α particle and two β particles, the resulting nucleus assumes the same atomic number, but the mass number decreases by four units. A radioactive decay of this type shown below produces isotopes

$$ {}^{218}_{84}\text{Po} \xrightarrow{-\alpha} {}^{214}_{82}\text{Pb} \xrightarrow{-\beta} {}^{214}_{83}\text{Bi} \xrightarrow{-\beta} {}^{214}_{84}\text{Po} $$

These three illustrations can be summarized as follows (Table 13.2).

TABLE 13.2. Illustration of group displacement law

Group	*13*	*14*	*15*	*16*	*17*
		${}^{214}_{82}\text{Pb}$	$\xleftarrow{-\alpha}$	${}^{218}_{84}\text{Po}$	
		$\xrightarrow{-\beta}$	${}^{214}_{83}\text{Bi} \xrightarrow{-\beta}$	${}^{214}_{84}\text{Po}$	

Exercise 13.1. Which one of the transmutations given below does not take place by α-decay ?

(*i*) ${}^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th}$ (*ii*) ${}^{227}_{89}\text{Ac} \longrightarrow {}^{223}_{87}\text{Fr}$

(*iii*) ${}^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn}$ (*iv*) ${}^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb}$

(*v*) ${}^{213}_{83}\text{Bi} \longrightarrow {}^{213}_{84}\text{Po}$

Solution. An α particle is a helium nucleus, ${}^{4}_{2}\text{He}$. Any equation which does not get balanced by adding ${}^{4}_{2}\text{He}$ will correspond to the transmutation which does not take by α-decay.

(*i*) ${}^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$; balances

(*ii*) ${}^{227}_{89}\text{Ac} \longrightarrow {}^{223}_{87}\text{Fr} + {}^{4}_{2}\text{He}$; balances

(*iii*) $^{226}_{88}Ra \longrightarrow ^{222}_{86}Rn + ^{4}_{2}He$; balances

(*iv*) $^{212}_{84}Po \longrightarrow ^{208}_{82}Po + ^{4}_{2}He$; balances

(*v*) $^{213}_{83}Bi \longrightarrow ^{219}_{84}Po + ^{4}_{2}He$; does not balance

The transmutation of $^{213}_{83}Bi$ into $^{213}_{84}Po$ does not take place by α-decay but by β-decay.

Exercise 13.2. Calculate the number of α and β particles emitted when thorium, $^{232}_{90}Th$ decay to lead, $^{208}_{82}Pb$.

Solution. $^{232}_{90}Th$ decays to $^{208}_{82}Pb$

Difference in atomic mass$=232-208=24$ amu

Number of α particles emitted to account for the loss$=\frac{24}{4}=6$.

Expected Z for the daughter element$=90-12=78$.

To attain $Z=82$, increase in Z required$=82-78=4$.

Hence, number of β-particles emitted to balance for this increase$=4$.

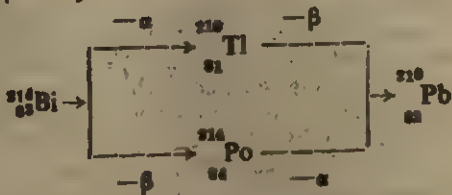
Thus, the transmutation of $^{232}_{90}Th$ into $^{208}_{82}Pb$ involves the following number of particles.

α Particles$=6$
β Particles$=4$

Exercise 13.3. The radioisotopic bismuth, $^{214}_{83}Bi$ decays by both α-emisson and β-emission. Name the two products formed. They further decay to the same isotope, $^{210}_{82}Pb$. What kind of emissions are involved in the two cases ?

Solution. The decay of $^{214}_{83}Bi$ into $^{210}_{82}Pb$ takes place by both

α-decay and β-decay. The scheme of the changes will be as follows.



Thus, the two products formed are $^{210}_{81}$Tl and $^{214}_{84}$Po. The types of emissions are shown in the decay scheme.

13.4. RADIOACTIVE DISINTEGRATION SERIES

The heavy radioactive elements disintegrate by a series of successive emissions of α and β particle and frequent adjustment of energy within the nucleus until a stable nuclide is formed. The stable end product is usually an isotope of lead ; occasionally bis-

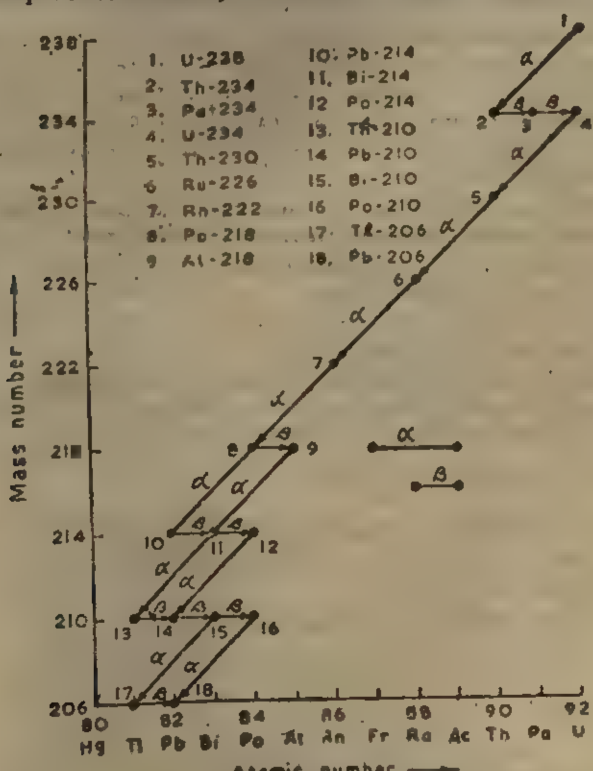


Fig. 13.6. The natural radioactive disintegration series of uranium-238.

muth. The disintegration of naturally occurring radioactive elements falls into three disintegration series, as given below, named after the most stable nuclide in each series. A fourth series, known as neptunium series, contains nuclides which do not occur naturally. Since mass number changes only by four units due to α-emission (natural radioactivity) they fit into one of the formulae : $4n$, $4n+1$, $4n+2$, $4n+3$. The respective series are :

$4n$ series : **Thorium series** starts from thorium-232 and ends in lead-208.

$4n+1$ series : **Neptunium series** begins with neptunium-237 and ends with bismuth-209.

$4n+2$ series : **Uranium series** begins with uranium-238 and ends with lead-206.

$4n+3$ series : **Actinium series** begins from uranium-235 and ends in lead-207.

The entire uranium series is shown in Fig. 13·6.

13.5. THE KINETICS OF NUCLEAR DECAY

The nuclear decay is a random process. The disintegration of a nucleus is totally independent of both its history and the decay of adjacent atoms. All radioactive atoms within a nuclide do not disintegrate simultaneously. All radionuclides have different stabilities and decay at different rates. However, an important observation has been made :

The rate of nuclear disintegration is proportional to the number of unstable nuclei present in the sample.

The rates of all radioactive decays are independent of temperature and obey first order kinetics. We have already seen that first-order processes occur at rates proportional only to the concentration of one reacting substance (Unit 6).

Using the symbolism of chemical kinetics and letting N be the number of parent nuclei in a given sample, the rate of decrease in the number of disintegrating atoms can be written as

$$\text{Rate of decay } = -\frac{dN}{dt} = \lambda N \qquad (13.1)$$

where λ is the decay or disintegration constant and t is the time.

A plot of the mass of an unstable nuclide against time gives a logarithmic curve (Fig. 13.7).

Equation (13.1) can be rewritten as,

$$\frac{dN}{dt} = -\lambda N$$

or

$$\frac{dN}{N} = -\lambda dt \qquad ...(13.2)$$

Integration of equation (13.2) leads to

$$\ln N = -\lambda t + C \qquad ...(13.3)$$

where C is a constant of integration.

Initially at time $t=0$, $N=N_0$. Substituting these values in the equation (13.3), we get,

$$\ln N_0 = C \qquad \text{...(13.4)}$$

By combining equations (13·3) and (13.4), we get,

$$\ln N = -\lambda t + \ln N_0$$

or $$\ln \frac{N}{N_0} = -\lambda t \qquad \text{(13.5)}$$

or $$\ln \frac{N_0}{N} = \lambda t$$

or $$\lambda = \frac{1}{t} \ln \frac{N_0}{N}$$

By converting natural logarithms to common logarithms, we get ;

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N} \qquad \text{...(13.6)}$$

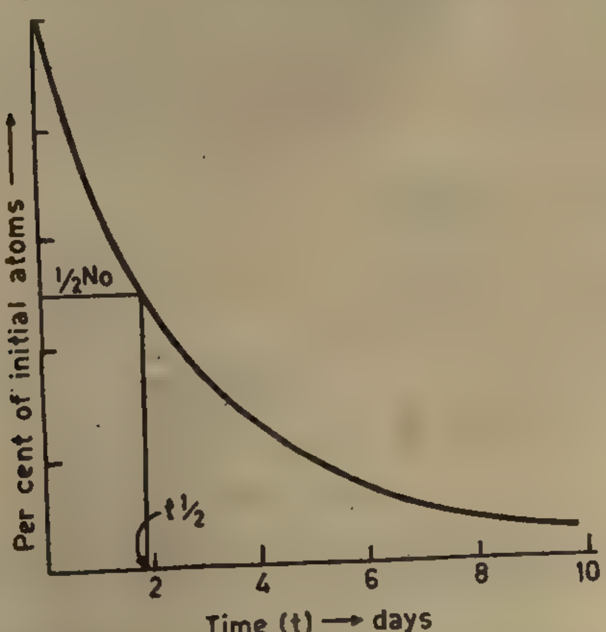


Fig. 13.7. Decay curve for an unstable nuclides ; the rate of decay of a unstable nuclide obeys first order kinetics

Equation (13.5) can also assume the form

$$\frac{N}{N_0} = e^{-\lambda t} \qquad \text{...(13.7)}$$

It follows from equation (13.7) that the number of radioactive atoms decreases exponentially with time.

Thus, it amounts to saying that the activity of the parent atom decays exponentially with time (Fig. 13.7).

Half-life Period

Because the decay curve (Fig. 13.7) is asymptoic to the *x*-axis, a radioactive nuclide never decays completely. To estimate the stability of an element (or compound or substance) the time taken for the entire mass to decay is not taken into consideration, but the **half-life**, $t_{\frac{1}{2}}$.

Half-life period is the time required for disintegration to one-half of the radioactive atoms present initially in the system.

The concept of half-life is illustrated well through Fig. 13.8, which shows that the residual amount of radioactive nuclide is reduced by half in every 3.8 days (radon-222 $t_{1/2}$=3·8 days).

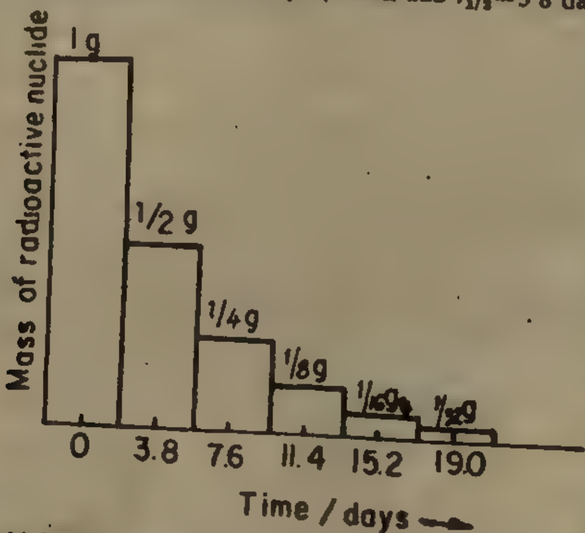


Fig. 13.8. Illustration of the concept of half-life. A radioactive element or material decays to one half of its original value in one $t_{\frac{1}{2}}$.

The half-life of a radioactive nuclide can be determined by counting the number of particles emitted, *i.e.*, by measuring the count rate (A_s)at intervals over a suitable time period. Scintillation counter, Wilson cloud chamber and Geiger Muller counter are the usual instruments used for the purpose.

Since radioactive decay is a first order process, we take into consideration the equation (13.5),

$$\ln \frac{N}{N_0} = -\lambda t$$

where N_0=number of unstable nuclei at the start
N=number of such nuclei after time, t.

After the half-time has elasped

$$\frac{N}{N_0} = \frac{1}{2}$$

and $t = \frac{1}{2}$

$$\therefore \quad t_{1/2} = \frac{\ln 2}{\lambda}$$

$$= \frac{2.303}{\lambda} \log 2$$

$$t_{1/2} = \frac{0.693}{\lambda} \quad \text{...(13.8)}$$

Thus, if the disintegration constant (λ) is known, the half-life period ($t_{1/2}$) of the radioactive nuclide can be calculated and vice versa. The half-life period, which is inversely proportional to the disintegration constant (λ), is thus independent of the amount of radioactive element initially present. The extent of decay of any radioactive element is independent of temperature, pressure and other physical conditions. The half-life periods of different elements vary widely from fraction of a second to million of years. (Table 13.3)

TABLE 13.3. Some half-life periods

Radioactive element	*Half-life*
Uranium—238	5×10^9 yr
Thorium—234	25 days
Protactinium—234	7 hr
Uranium—234	2.7×10^5 yr
Radium—226	1.6×10^3 yr
Polonium—218	3 min
Polonium—210	5 days
Carbon—14	5760 yr
Thorium—234	7.6×10^4 yr
Lead—210	22 yr

Graphic calculation of λ and $t_{1/2}$

Consider the equation (13.7)

$$\frac{N}{N_0} = e^{-\lambda t}$$

On rearranging the equation (13.7),

$$N = N_0 \, e^{-\lambda t}$$

and differentiating with respect to t,

$$\frac{dN}{dt} = -\lambda N_0 \, e^{-\lambda t}$$

or $$-\frac{dN}{dt} = \lambda N_0 \, e^{-\lambda t} \quad ...(13.9)$$

Taking logarithms of equation (13.9), we get,

$$\ln\left[-\frac{dN}{dt}\right] = \ln(\lambda N_0) - \lambda t \quad ...(13.10)$$

Now if we assume that the corrected detector count rate (A'_s) is equal to the rate of decay, *i.e.*,

$$A'_s = -\frac{dN}{dt} \quad ...(13.11)$$

By substituting in equation (13.10), we get,

$$\ln A'_s = \ln(\lambda N_0) - \lambda t \quad ...(13.12)$$

Since both λ and N_0 are constants, the equation (13.12) can assume the form

$$y = mx + C$$

and a graph of $\ln A'_s$ versus t should be a straight line of gradient $-\lambda$, Hence λ (represents the proportion which decays each second) can be known and by using equation (13.8) a value for $t_{1/2}$ can be estimated.

Units of radioactivity. The SI unit of radioactivity is the bacqueral (Bq), defined as one disintegration per second. The activity of any nuclide can be calculated from its half-life.

The activity of 1 g of radium-226 ($3{\cdot}7 \times 10^{10}$ disintegration per second) was earlier used as a unit of radioactivity called the '**curie**''

i.e., 1 Curie$=3{\cdot}7 \times 10^{10}$ disintegration per second

1 Curie$=3{\cdot}7 \times 10^{10}$ Bq

Exercise 13:4. The half-life for the decay of U-238 to Th-234 is $4{\cdot}5 \times 10^9$ yr. How many α particles are produced per second in a sample containing 2×10^{10} atoms of U-238.

Solution. By putting the value of $t_{1/2}$ in the equation (13.8), we get,

$$\lambda=\frac{0.693}{4.5\times 10^{9}\text{yr}}=1.5\times 10^{-10}\text{ yr}^{-1}$$

By using equation, given below for rate of decay we calculate for the rate of decay.

Rate of decay $=\lambda N$

Rate of decay $=(1.5\times 10^{-10}\text{ yr}^{-1})\ 2\times 10^{20}$ atoms

$=3.0\times 10^{10}$ atoms yr^{-1}

One α particle is emitted for every atom that decays. Thus, the rate of α particle production is as follows.

Rate of decay $=3\times 10^{10}$ α particles yr^{-1}

$$=3\times 10^{10}\alpha\text{ particles}\times\frac{1\text{ yr}}{365\text{ days}}\times\frac{1\text{ day}}{24\text{ hr}}$$

$$\frac{1\text{ hr}}{60\text{ min}}\times\frac{1\text{ min}}{60\text{ s}}$$

$=960$ α particles s^{-1}.

Exercise 13.5. A radioactive element disintegrates at such a rate that after 100 min only 1/4 of the original amount remains. Calculate the decay constant and the half-period.

Solution. According to the equation,

$$\lambda=\frac{2.303}{t}\log\frac{N_0}{N}$$

Now $t=100$ min ;

$$N_0=1\ ;\ N=\frac{1}{4}$$

Putting these values in equation ;

$$\lambda=\frac{2.303}{100}\log\left(\frac{1}{\frac{1}{4}}\right)\text{ min}^{-1}$$

$$\lambda=0.0138\text{ min}^{-1}$$

Now the half-life period is given by the expression,

$$t_{1/2}=\frac{0.693}{\lambda}$$

$$t_{1/2}=\frac{0.693}{0.0138}=50\text{ min}$$

13.6. NUCLEAR REACTIONS (TRANSMUTATIONS)

A nuclear reaction is different from a chemical reaction. In a chemical reaction, only rearrangement of extranuclear electrons takes place. The atomic nucleus is not involved and remains unaffected. However, in a nuclear reaction, a rearrangement of protons and neutrons in the nucleus of the atom takes place and new atomic species are produced. This change is accompanied by the release of energy. There are two types of nuclear reactions :

(*i*) That in which a radioactive nuclide (unstable) decays spontaneously giving a more stable nucleus. This is the basis of natural radioactivity or radioactive decay (already discussed).

(*ii*) That in which change is effected artificially, by the collision of two nuclei. It is this type of nuclear reaction that will be discussed in the following sections. Many new heavy elements as well as medically useful isotopes have been produced in this manner.

13.6.1. Artificial Transmutation of Elements

Transmutation is a process of converting of one element into another. The facts of radioactivity immediately brings to mind the questions :

(*i*) Can the atoms of those elements which are not radioactive be broken down by artificial means into atoms of simpler elements ?

(*ii*) Can atoms of the simpler atoms be built up into more complex atoms ? In either case, a transmutation of the element would result.

Some success in transmutation has been achieved by means of collision of the stable nuclei with high speed particles like α particles, neutrons, protons, deuterons *etc.* In 1919, Rutherford allowed a beam of α particles from a radioactive source to pass through nitrogen gas. As a result of inter collission, a nuclear reaction that produced O—17 and a proton took place.

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$$

Because of a strong repulsion between positively charged nuclei of nitrogen and positively charged helium nuclei, transmutation was found to be limited. On bombarding the beryllium-9 with α particles (Bothe and Becker 1930) a new fast moving particle with high penetrating power was produced. This is the reaction in which the neutron was first identified by Sir James Chadwick (1932).

$$^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ^{1}_{0}n$$

Later neutron was used for other transmutations. Since the time of Rutherford, thousand of isotopes have been prepared by nuclear reactions.

$$^{209}_{83}Bi + ^{2}_{1}H \longrightarrow ^{210}_{84}Po + ^{1}_{0}n$$

$$^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P + ^{1}_{0}n$$

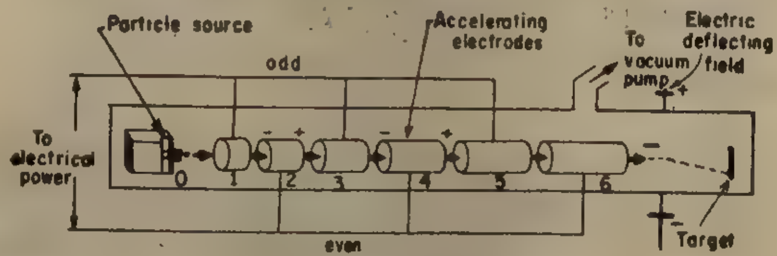
(Radioactive)

In a nuclear reaction, since the nucleus (target) has a positive charge and many of the bombarding particles or nuclei (called projectiles) alsɔ have positive charge, the particles must have a high kinetic energy to overcome the natural repulsion between these two like charges particles. Because of the inter-collision between the target and the projectile, a high energy nucleus is formed which in turn, emits a new particle (usually a neutron) formings a new product. This new particle carries away the excess energy from the collision.

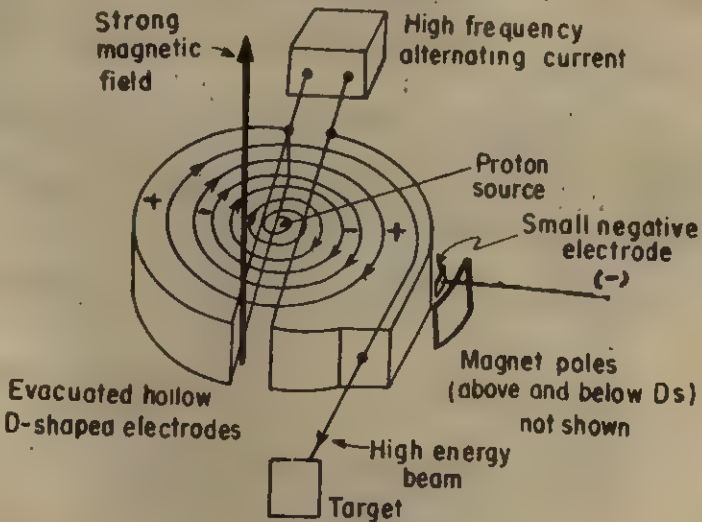
$$ {}^{14}_{7}N + {}^{4}_{2}He \xrightarrow{\text{slow}} {}^{18}_{9}F \xrightarrow{\text{Fast}} {}^{17}_{8}O + {}^{1}_{1}H $$

(Unstable)

The invention of **particle accelerators** (Fig. 13.9) which accelerate particles to high velocities and energies has opened



(a) Linear accelerator,



(b) The cyclotron

Fig. 13.9. Particle accelerators

up vast possibilities for artificial nuclear reactions. Table 13.4 lists some of these accelerators.

TABLE 13.4. Acceleration of particles

Type of accelerator	*Particles accelerated*	*Maximum energy (Mev)*
Linear	${}^{1}_{1}H$, ${}^{4}_{2}He$	1—1000
Cyclic cyclotron	${}^{1}_{1}H$, ${}^{2}_{1}H$ ${}^{4}_{2}He$	25
Synchrocyclotron	${}^{1}_{1}H$, ${}^{2}_{1}H$ ${}^{4}_{2}He$	500
Synchrotron	electrons, ${}^{1}_{1}H$	8000
Betatron	electrons	340

Neutrons, because they do not have to be accelerated, are particularly useful as projectiles. The neutrons which are emitted are fast neutrons, and have been effective in initiating further nuclear changes. Along with the product, other particles are also emitted, *e.g.*,

$${}^{14}_{7}N+{}^{1}_{0}n \longrightarrow {}^{14}_{6}C+{}^{1}_{1}H \qquad \text{(n, p) reaction}$$

Nuclear reactions are classified according to the projectiles that is used and the particle or radiation that is emitted. The reaction N-14 and α particles is an is an (α, p) reaction, because α particles are used as projectiles and protons are ejected. The following nuclear reactions illustrate a few of them.

$${}^{6}_{3}Li+{}^{1}_{0}n \longrightarrow {}^{4}_{2}He+{}^{3}_{1}T \qquad =2 \text{ tritium ; (n, t) reaction}$$

$${}^{28}_{14}Si+{}^{2}_{1}H \longrightarrow {}^{29}_{15}P+{}^{1}_{0}n \qquad {}^{2}_{1}H\text{=deuteron ; (d, n) reaction}$$

$${}^{23}_{11}Na+{}^{2}_{1}H \longrightarrow {}^{24}_{11}Na+{}^{1}_{1}H \qquad \text{(d, p) reaction}$$

$${}^{55}_{25}Mn+{}^{1}_{1}H \longrightarrow {}^{55}_{26}Fe+{}^{1}_{0}n \qquad \text{(p, n) reaction}$$

$$^{209}_{83}Bi + ^{4}_{2}He \longrightarrow ^{211}_{85}At + 2\,^{1}_{0}n \qquad (\alpha,\ 2n) \text{ reaction}$$

$$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{7}_{4}Be + ^{1}_{0}n \qquad (p,\ n) \text{ reaction}$$

(Electron capture)

$$^{31}_{15}P + ^{2}_{1}H \longrightarrow ^{32}_{15}P + ^{1}_{1}H \qquad (d,\ p) \text{ reaction}$$

(β^- emission)

$$^{14}_{7}N + ^{1}_{1}H \longrightarrow ^{15}_{8}O + \gamma \qquad (p,\ \gamma) \text{ reaction}$$

(β^+ emission)

$$^{127}_{53}I + ^{1}_{0}n \longrightarrow ^{128}_{53}I \qquad \text{(Neutron capture)}$$

Artificial Radioactivity

It has been found that the bombardment of nuclei of some of the elements results in the formation of radioactive isotopes of elements which disintegrate spontaneously. For example, aluminium on bombarding with α particles gives an isotope of phosphorus.

$$^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P + ^{1}_{0}n$$

(Radioactive)

This radioactive isotope of phosphorus disintegrates with emission of positron.

$$^{30}_{15}P \longrightarrow ^{30}_{14}Si + ^{0}_{+1}e$$

This isotope of phosphorus (P-30 ; $t\frac{1}{2}$=2·5 min) is said to be artificially radioactive since it has been obtained by artificial means. This was thus the first case of **induced radioactivity**. However, this radioactivity was not induced on aluminium but it came from the daughter element $^{30}_{15}P$.

$^{30}_{15}P$ was the first artificially produced radioactive nuclide. Since then more than 1000 new radioactive nuclides have been produced and studied. Artifically radioactive elements behave very much similar to naturally radioactive elements. They decay according to the same rate law.

Artificially radioactive elements have proved to be effective therapeutic agents. Because of their short half-life periods, they offer certain advantages in the treatment of diseases. They find uses in studying the metabolism of plants and animals. ${}^{60}_{27}Co$ is used in cancer therapy. There have been a great deal of application of these synthefic radioactive isotopes in the field of medicine, mainly in the area of diagnosis of diseases. More examples for the preparation of radioactive isotopes are given below :

1. $${}^{127}_{53}I + {}^{1}_{0}n \longrightarrow {}^{128}_{53}I + \gamma$$

(Radioactive ; $t_{\frac{1}{2}}$ 25 min)

$${}^{128}_{53}I \longrightarrow {}^{128}_{54}Xe + {}^{0}_{-1}e$$

2. $${}^{59}_{27}Co + {}^{1}_{0}n \longrightarrow {}^{60}_{27}Co$$

(Radioactive ; $t_{\frac{1}{2}}$ 5.27 years)

$${}^{60}_{27}Co \longrightarrow {}^{60}_{28}Ni + {}^{0}_{-1}e$$

3. $${}^{35}_{17}Cl + {}^{1}_{0}n \longrightarrow {}^{35}_{16}S + {}^{1}_{1}H$$

(radioactive ; $t_{\frac{1}{2}}$ 87 days)

$${}^{35}_{16}S \longrightarrow {}^{35}_{17}Cl + {}^{0}_{-1}e$$

Radioactive isotopes of every known elements have been artifically prepared.

13.7. SYNTHETIC ELEMENTS

Elements 43, 61, 85 and 87 were for years blank spaces in the periodic table. These elements do not occur in nature except briefly during a natural decay series. These elements have now been produced in small amounts by nuclear reactions. Their preparation filled the gaps in the periodic table between hydrogen and uranium. Particle accelerators have been vary helpful in the preparation of new, heavy elements. In fact, all the elements from atomic number 93 to 106, 107 (both not yet named) are synthetic elements.

The first transuranium element, that is element with atomic number 93 was synthesized at the University of California in 1940

by Edwin McMillan and P.H. Abelson. The bombardment of U—238 with neutrons produced a radioactive isotope U—238 which on β—1 emission yielded element 93.

$$^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U - 239 \text{(neutron capture)}$$

(Radioactive)

$$^{239}_{92}U \longrightarrow {}^{239}_{93}Np + {}^{0}_{-1}e + \nu^-$$

This new element was named **neptunium** because of its placement next to uranium, just as the planet Neptune is adjacent to the planet Uranus. Element with atomic number 94 was produced by the decay of Np—238 which was formed by bombarding U—238 with deuterons.

$$^{238}_{92}U + {}^{2}_{1}H \longrightarrow {}^{238}_{93}Np + 2\,{}^{1}_{0}n$$

(Radioactive)

$$^{238}_{93}Np \longrightarrow {}^{238}_{94}Pu + {}^{0}_{-1}e + \nu^-$$

This element was named plutonium, Pu after the planet Pluto, which is just beyond Neptune.

Since atoms are conserved in chemical reactions, it is obvious that usual chemical reactions cannot be the route to new elements. In Table 13·5, several nuclear reactions that have been used to prepare transuranic elements have been summarized. For these elements, not a single stable isotope has been reported. Their isotopes have very short half-lives. We have already discsused the chemistry of transuranic elements briefly in Unit 11. It follows by analogy of lanthanides, that beginning with actinium (atomic number 89), a second group of elements will fill up level 5.

TABLE 13.5. Typical nuclear reactions used tor prepare the transuranium elements

Element	*Isotope*	*Half-life*	*Nuclear reaction*
Neptunium	$^{239}_{93}Np$	2·35 days	$^{238}_{92}U + {}^{1}_{0}n \longrightarrow \left[{}^{239}_{92}U\right] + \gamma$
			$\left[{}^{239}_{92}U\right] \longrightarrow {}^{239}_{93}Np + \beta$

Element	*Isotope*	*Half-life*	*Nuclear reaction*
Plutonium	$^{238}_{94}Pu$	89yr	$^{238}_{92}U + ^{2}_{1}H \longrightarrow \left[^{238}_{93}Np\right] + 2\,^{1}_{0}n.$
			$\left[^{238}_{93}Np\right] \longrightarrow ^{238}_{94}Pu + \beta$
	$^{239}_{94}Pu$	24,360 yr	$^{238}_{92}U + \alpha \longrightarrow ^{239}_{94}Pu + 3\,^{1}_{0}n$
Americium	$^{240}_{95}Am$	51 hr	$^{239}_{94}Pu + \alpha \rightarrow ^{240}_{95}Am + ^{1}_{1}H + 2\,^{1}_{0}n$
	$^{241}_{95}Am$	458 yr	$^{240}_{94}Pu + ^{1}_{0}n \longrightarrow \left[^{241}_{94}Pu\right] + \gamma$
			$\left[^{241}_{94}Pu\right] \longrightarrow ^{241}_{95}Am + \beta$
Curium	$^{242}_{96}Cm$	163 days	$^{239}_{94}Pu + \alpha \longrightarrow ^{242}_{96}Cm + ^{1}_{0}n$
Berkelium	$^{243}_{97}Bk$	4.5 hr	$^{241}_{95}Am + 1\alpha \longrightarrow ^{243}_{97}Bk + 2\,^{1}_{0}n$
Californium	$^{246}_{98}Cf$	35.7 hr	$^{238}_{92}U + ^{12}_{6}C \longrightarrow ^{246}_{98}Cf + 4\,^{1}_{0}n$
Einsteinium	$^{247}_{99}Es$	5.0 min	$^{238}_{92}U + ^{14}_{7}N \longrightarrow ^{247}_{99}Es + 5\,^{1}_{0}n$
Fermium	$^{249}_{100}Fm$	2.5 min	$^{238}_{92}U + ^{16}_{8}O \longrightarrow ^{249}_{100}Fm + 5\,^{1}_{0}n$
Mendelevium	$^{256}_{101}Md$	1.5 hr	$^{253}_{99}Es + \alpha \longrightarrow ^{256}_{101}Md + ^{1}_{0}n$
Nobelium	$^{254}_{102}No$	50 s	$^{246}_{96}Cm + ^{12}_{6}C \longrightarrow ^{254}_{102}No + 4\,^{1}_{0}n$
Lawrencium	$^{257}_{103}Lw$	8 s	$^{252}_{98}Cf + ^{10}_{5}B \longrightarrow ^{257}_{103}Lw + 5\,^{1}_{0}n$
			$^{250}_{98}Cf + ^{11}_{5}B \longrightarrow ^{257}_{103}Lw + 4\,^{1}_{0}n$

Element	Isotipe	Half-life	Nuclear reaction
*Rutherfordium	$^{257}_{104}Rf$	4·8 s	$^{249}_{98}Cf + ^{12}_{6}Cf \longrightarrow ^{257}_{104}Rf + 4\,^{1}_{0}n$
	$^{259}_{104}Rf$	~3 s	$^{249}_{98}Cf + ^{13}_{6}C \longrightarrow ^{259}_{104}Rf + 3\,^{1}_{0}n$
*Hahnium	$^{260}_{105}Ha$	1.6 s	$^{249}_{98}Cf + ^{15}_{7}N \longrightarrow ^{260}_{105}Ha + 4\,^{1}_{0}n$
	$^{263}_{106}X$	0.9 s	$^{249}_{98}Cf + ^{18}_{8}O \longrightarrow ^{263}_{106}X + 4\,^{1}_{0}n$

*Proposed names.

13.8. NUCLEAR FISSION

The phenomenon of nuclear fission, *i.e.*, splitting of atomic nuclei, started with the work of the Italian physicist Enrico Fermi in 1934. Fermi bombarded uranium-235 atoms with slow moving neutrons in the hope that the neutrons would be captured in the nucleus so that new elements, heavier than uranium, might be synthesized. He hypothesized that neutron capture might lead to beta emission and the formation of new elements with a higher mass number. The results, however, were surprisingly different.

In 1938, two German scientists Otto Hahn and Fritz Strassmann repeated Fermi's reaction and analyzed the products. Much to their surprise, they found a number of known elements with atomic numbers between those of zinc (Z=30) and terbium (Z=65) (Fig. 13.10).

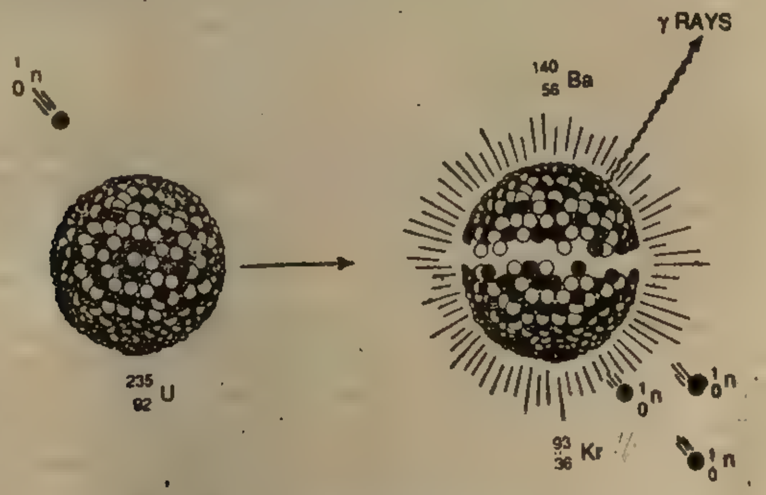


Fig. 13.10. A diagrammatic representation of the fission of uranium-235 nucleus

$$
{}^{235}_{92}\mathrm{U}+{}^{1}_{0}\mathrm{n} \longrightarrow \left[{}^{236}_{92}\mathrm{U}\right] \longrightarrow
\begin{cases}
{}^{140}_{56}\mathrm{Ba}+{}^{93}_{36}\mathrm{Kr}+3\,{}^{1}_{0}\mathrm{n}+\text{energy} \\
{}^{144}_{54}\mathrm{Xe}+{}^{90}_{38}\mathrm{Sr}+2\,{}^{1}_{0}\mathrm{n}+\text{energy} \\
{}^{144}_{55}\mathrm{Cs}+{}^{90}_{37}\mathrm{Rb}+2\,{}^{1}_{0}\mathrm{n}+\text{energy.}
\end{cases}
$$

$$
{}^{235}_{92}\mathrm{U}+{}^{1}_{0}\mathrm{n} \longrightarrow {}^{95}_{42}\mathrm{Mo}+{}^{139}_{57}\mathrm{La}+2\,{}^{1}_{0}\mathrm{n}+7\,{}^{0}_{-1}\mathrm{e}
$$

$$
{}^{235}_{92}\mathrm{U}+{}^{1}_{0}\mathrm{n} \longrightarrow {}^{94}_{38}\mathrm{Sr}+{}^{139}_{54}\mathrm{Xe}+3\,{}^{1}_{0}\mathrm{n}+\text{energy}
$$

Of the natural nuclides only U-235 undergoes fission when bombarded by a neutron. The U-235 nuclide captures the neutron, which in turn supplies enough energy to overcome the activation energy barrier and produce the fission reaction. The highly activated intermediate U-236 can cleave in many ways, depending on its energy level. The nuclear fission just discussed has been induced by thermal neutrons and the fission fragments are variable. Uranium-235 can also spontaneously decay into two fragments. This type of

$$
{}^{235}_{92}\mathrm{U} \longrightarrow {}^{140}_{56}\mathrm{Ba}+{}^{92}_{36}\mathrm{Kr}+3\,{}^{1}_{0}\mathrm{n}
$$

fission is not common. Induced fission of U—235 gives about 200 radioactive products (ranging Z=30 to Z=65). Most of the fission fragments are neutron excessive relative to the stable nucleus of the same mass number ; for this reason they disintegrate by a series of β-emmission process until they are transmuted into a stable nucleus.

Besides thermal neutrons, any particle with sufficient energy can cause a nucleus to fission. Even γ-ray induced fission is a well known process. Neutron-induced fission has assumed importance because more neutrons are produced for each neutron that is consumed by a reaction. Each of produced neutrons can initiate another fission. This means that a **chain reaction** can be initiated that could produce tremendous amounts of energy. This is illustrated in Fig. 13.11.

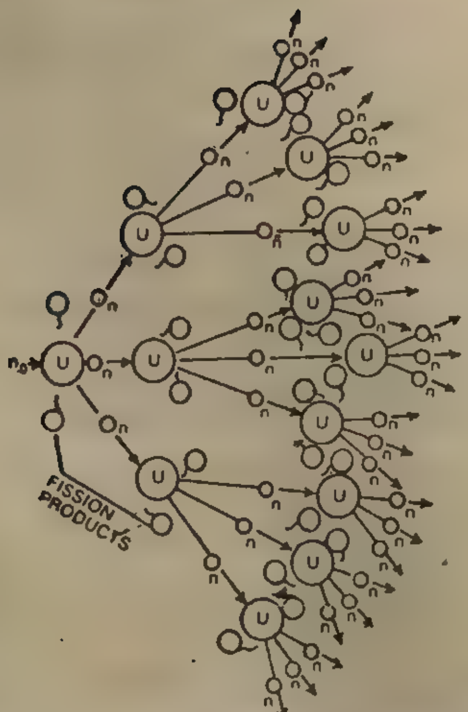


Fig. 13.11. Fission of uranium and the chain reaction. The neutron is absorbed by unamium-235 nucleus which fissions and produces fission fragments and more neutrons. These neutrons induce the fission of other U-235 nuclei

Natural uranium contains two isotopes U-235 and U-238. Experiment showed tat U-235 (rater isotope) is mainly responsible for the vast release of energy during fission. Uranium-238 absorbs neutrons and disintegrates to neptunium and plutonium.

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{92}U + \gamma$$

$$^{239}_{92}U \rightarrow ^{239}_{93}Np + ^{0}_{-1}e$$

$$^{239}_{93}Np \rightarrow ^{239}_{94}Pu + ^{0}_{-1}e$$

The plutonium-239 which is formed undergoes atomic fission similar to U-235.

The amount of energy released when a nucleus is split is enormous. The sum of the masses of the fissioned atoms and neutrons produced is less than the mass of the target atom (say uranium U-235). The lost mass is converted into energy according to the Einstion equation, $E=mc^2$.

Consider the reaction :

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{94}_{38}Sr + ^{139}_{54}Xe + 3\,^{1}_{0}n + \text{energy}$$

Now to calculate the Δm,

$\Delta m = \Sigma(\text{mass})$ products$-\Sigma(\text{mass})$ reactants

$$=[93.9154+138.9178+3(1.0087)-235.0439-1.0087]\ \text{amu}$$
$$=-0.1933\ \text{amu per atom}$$

or
$$=-0.1933\ \text{g mol}^{-1}$$
$$=1.933\times10^{-4}\ \text{kg mol}^{-1}.$$

The energy liberated in the process would be

$$E=mc^2$$
$$=(1.933\times10^{-4}\ \text{kg mol}^{-1})\ (2.998\times10^{8}\ \text{ms}^{-1})^2$$
$$=1.737\times10^{13}\ \text{kg m}^2\ \text{s}^{-2}\ \text{mol}^{-1}$$
$$=1.737\times10^{13}\ \text{J mol}^{-1}\ (\text{Since } 1\ \text{kg m}^2\ \text{s}^{-2}=1\ \text{J})$$

or
$$=1.737\times10^{10}\ \text{kJ mol}^{-1}.$$

This enomorus release of energy by the fission of one mole of uranium-235 atoms gives some idea about the energy changes that are associated with nuclear reactions.

The energy released in nuclear reaction being very large is usually expressed in terms of mega electron volts denoted by MeV. In SI units,

1 MeV	$=1.622\times10^{-13}$ J
1 atomic mass unit (amu)	$=1.6603\times10^{-27}$ kg
	$=2.9979\times10^{8}$ m/s

Substituting these values in expression $E=mc^2$, we obtain

$$1\ \text{amu}=1.6603\times10^{-27}\ \text{kg}\times(2.9979\times10^{8}\ \text{m/s})^2$$
$$=1.4924\times10^{-10}\ \text{kg m}^2/\text{s}^2$$
$$=\frac{1.4924\times10^{-10}\ \text{J}}{1.622\times10^{-19}\ \text{J/eV}}=931.48\times10^{6}\ \text{eV}$$
$$=931.48\ \text{MeV}.$$

In the reaction just discussed the Δm is 0.1933 amu Since, amu=931.48 MeV, for every uranium atom undergoing fission, the energy released is,

$$=0.1933\times931.48\ \text{MeV}$$
$$=180.06\ \text{MeV}.$$

The evolution of tremendous amount of energy has been ascribed to a chain reaction. The nuclear chain reaction is self-sustaining as during fission of U-235 nucleus neutrons (more than one) are

produced. It means the reaction generates the means to trigger additional electrons. In practice, however, the fission of a small piece of U-235 is not self-sustaining because many neutrons are lost to the environment. Further U-238 (exist with U-235) being a non-fissionable isotope can prohibit the fission chain reaction of the U-235 from occurring by absorbing the emitted neutrons. Hence an adequate quantity of U-235 must be available to absorb the neutrons. The minimum quantity to sustain the chain reaction is called the **critical mass.**

13.8.1. Atomic Bomb

A critical mass (or critical size) of U-235 is necessary for a chain reaction to be self-perpetuating and for an explosion to take place. If the critical mass is contained in a small enough volume, the ratio of the surface area to volume decreases. As a result, the emitted neutrons are captured before escaping

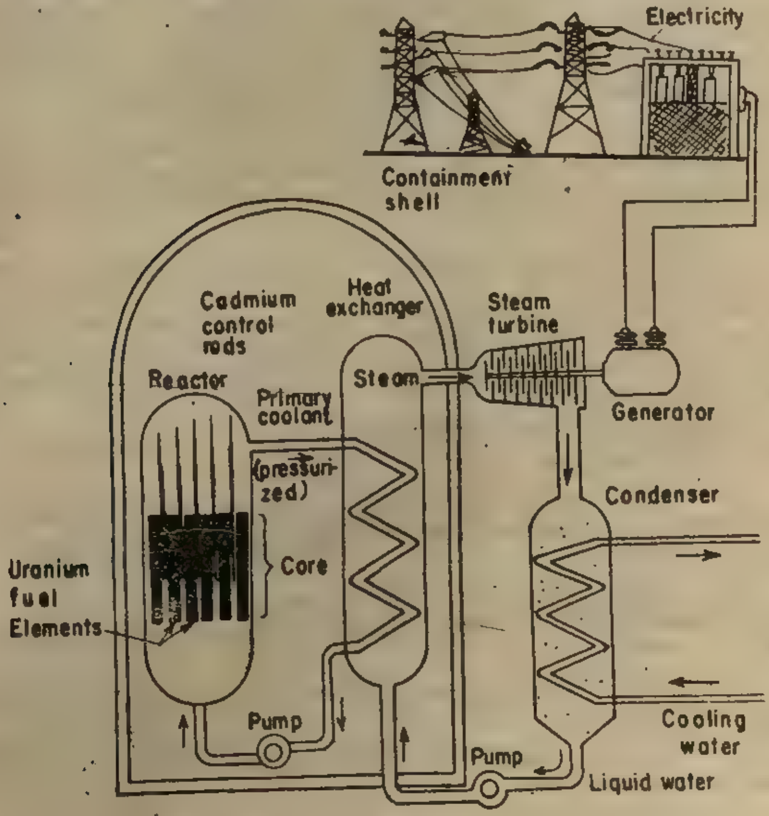


Fig. 13.12. A nuclear rector.

through the surface which collide with other fissionable atoms to sustain and expand the process. In producing an atomic bomb, it seems logical that pieces of subcritical masses of a fissionable nuclide are brought together into a supercritical mass. This can done by an ordinary chemical explosive such as trinitrotoluence (TNT). An uncontrolled nuclear fission explosion results releasing enormous amount of energy.

13 8.2. Nuclear Reactor

This enormously destructive device, however, can be tamed. The equipment in which the chain reaction can proceed in a controlled manner is called **a nuclear reactor** (Fig. 13.12). A reactor consists of :

(*a*) a fissionable material (uranium enriched in U-235) just slightly larger than a critical mass (there is far less fissionable material per unit volume) than there is in an atomic bomb.

(*b*) control rods made of a substance that absorbs neutrons efficiently, such as cadmium, boron steel *etc*. The fissionable material (called fuel elements) is interspersed with control rods. Control rods slow down the rate of fission by absorbing neutrons.

(*c*) a moderator, that surrounds the fuel rods, slows down the emitted neutrons to thermal speeds so that they are more readily captured by another fissionable nucleus. Graphite and heavy water (D_2O) are all good moderators.

The large amount of energy produced in the nuclear reactor appears primarily as heat, which is used in the production of electrical power. The heat removed from the reactor is used to convert water to steam, which is then used to drive turbines that generate electricity. Nuclear reactors are used to power military ships, particularly submarines.

Some nuclear power plants are already generating electricity at the following places :

1. Tarapur Atomic Power Staion in Maharashtra. Its capacit is 420 MW. It is the first station in India. It was commissioned i October 1969.

2. The Rajasthan Atomic Power Station at Rana Pratap Sagar near Kota (440 MW installed capacity)—one unit is operating since December 1973.

3. Madras Atomic Power Station at Kalpakkam (470 MW installed capacity).

4. Narora Atomic Power Station at Bulandshahr in Uttar Pradesh (470 MW installed capacity).

India aims at achieving an installed capacity of 10,000 MW b 2000 AD.

The following centres produce the fuel used in the atomic power stations and atomic reactors :

1. The Uranium Corporation of India Ltd., at Jaduguda in Bihar. The corporation is busy in mining the ore of uranium from which it is extracted.

2. Nuclear Fuel Complex at Hyderabad. It produces fuel elements for nuclear power reactors.

The heavy water (D_2O) used as coolant and moderator in power reactors is produced at Kota, Baroda, Nangal, Talcher and Tuticorin.

13.8.3. Breeder Reactors

Nuclear reactors are also a good source of neutrons for producing synthetic nuclei by neutron-capture reaction. As with our supply of fossil fuels, there is only a limited supply of the fissionable U-235, and nuclear reactors would face a somewhat uncertain future if not possible to produce other fissionable isotopes.

It is possible to build reactors, called **breeders reactors**, that not only generate large quantities of heat from fission, but also generate more fuel than they consume. In such reactors, some of the control rods are replaced with rods containing U-238 (or thorium). Some of the neutrons produced in the fission reaction are absorbed by the U—238 and give the reaction.

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow \underset{\text{Radioactive}}{\left[^{239}_{92}U \right]} \longrightarrow ^{239}_{93}Np + ^{0}_{-1}e$$

$$^{239}_{93}Np \longrightarrow ^{239}_{94}Pu + ^{0}_{-1}e$$

Pu—239 is fissionable.

$$^{239}_{94}Pu + ^{1}_{0}n \longrightarrow \text{fission products} + 2 \text{ or } (3\ ^{1}_{0}n)$$

Similarly, the naturally more abundant thorium-232 isotope can be used to breed the fissionable isotope, uranium-233.

However, the design of the breeder reactor has several difficulties associated with it This reactor requires the use of fast neutrons, so no moderator is needed, but control is more difficult. Here water is not used as coolant as the reactor operates at high temperatures. Liquid sodium is used as coolant which is not a neutron moderator. Sodium attacks the walls of the container particularly at high temperatures. At —915K Pu-239 metls, and hence, the effective dissipation of heat is required.

13.9. NUCLEAR FUSION

Fusion is the union of two light nuclei to form a heavier nucleus. It is quite opposite of nuclear fission. It is accompanied by large conversions of mass into energy.

Some examples of nuclear fusion reactions and the energy released in each process is shown below :

Fusion reaction	*Mass decrease*	*Energy released* (kJ/mol *He*)
$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{4}_{2}He$	0.026	23×10^{8}
$^{3}_{1}H + ^{2}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$	0.012	1.72×10^{9}
$4\,^{1}_{1}H \longrightarrow ^{4}_{2}He + 2\,^{0}_{+1}e$	0.029	26×10^{8}

Fusion reactions possess a high energy of activation mainly because of the electrostatic repulsion between the two nuclei that combine together. As a result, they occur only at extremely high temperatures where their kinetic energies are sufficient to overcome this repulsion. It is estimated that for such reactions (also called thermonuclear reactions) temperatures of approximately 200 million kelvins are needed.

The energy obtained from one fusion reaction is sufficient to cause other reactions to occur ; thus a chain reaction is set up, resulting in a thermonuclear explosion.

$$^{1}_{1}H + ^{1}_{1}H \longrightarrow ^{2}_{1}H + ^{0}_{1}e$$

$$^{2}_{1}H + ^{1}_{1}H \longrightarrow ^{3}_{2}He + \gamma$$

$$^{3}_{2}He + ^{3}_{2}He \longrightarrow ^{4}_{2}He + 2\,^{1}_{1}H$$

The sun derives its energy from the fusion of hydrogen nuclei into helium nuclei. In the sun, the temperature is about 10^{7} K and hydrogen nuclei have sufficient energy to fuse.

Fusion of deuterium and tritium isotopes of hydrogen, at very high temperatures is the source of energy in the hydrogen bomb.

As the fusion reactions require very high temperatures (100—200 million kelvins), such reactions were impossible prior to the development of fission reactions. So the development of the atomic bombs paved the way for the development of the hydrogen bomb. The hydrogen bomb has never been used in war as the destruction caused by it would be highly catastrophic.

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n + \text{Energy}$$

Deute- Tritium Helium Neutron
rium

This change is accompanied by a conversion of a portion of the mass into energy and is the nuclear reaction of the hydrogen bomb.

Fusion reactions are attractive energy sources, because the fuel, *i.e.*, hydrogen-2 is present together with the normal hydrogen, $^{1}_{1}H$ in all natural compounds of hydrogen, *e.g.*, water. It is therefore an inexhaustible and a more readily accessible starting material than uranium-235. This is why the fusion process is expected eventually to replace fission as the source of nuclear energy for future generations. It is impossible to predict, when, or indeed if ever, controlled fusion will be achieved. The major problem of achieving high temperatures to initiate the fusion reaction has still to be solved. Currently efforts are being made to use multiple high energy lasers to provide the high temperatures required to sustain the fusion reaction. With the technological advances, it is expected that nuclear fusion energy may become economically feasible before the end of this century. With the threatened exhaustion of the fossil fuel supply, a controlled fusion reaction is a potential energy source for the future.

There are several advantages of fusion reactions as an energy source when compared with fission reactions.

1. The energy produced per mole of nuclide from the fusion reaction is much greater than the fission reaction.

2. The fusion reaction is self-sustaining in character. The energy produced initially as the fusion reaction begins, can provide the activation energy for additional fusion reactions.

3. The necessary fuel, *i.e.*, hydrogen-2 for fusion reactions is available in abundance in ocean water.

4. The fusion reaction do not produce radioactive waste products that fission reactions do.

Exercise 13 6. Calculate the energy released by the nuclear fission of 1 kg of uranium—235. The fission reaction releases 3.20×10^{14} kJ of energy per nucleus fissioned.

Solution. Energy released per nucleus fissioned $= 3.20 \times 10^{4}$ kJ

Molar mass of uranium—235 = 235 g/mol

Mass of uranium—235 = 1 kg = 1000 g

Nuclei per mole $= 6.02 \times 10^{23}$

Total energy released

$$= 3.20 \times 10^{-14} \text{kJ} \times \frac{6.02 \times 10^{23}}{235} \times 1000$$

$$= 8 \times 10^{10} \text{ kJ}$$

13.10 APPLICATIONS OF RADIOACTIVITY AND RADIO-ISOTOPES

Radioactive nuclides find various applications either because they decay at known rates, or, in some cases, simply because they emit radiation continuously.

1. **Radio carbon dating.** The cosmic says initiate some nuclear changes within the realm of their penetration. In the upper atmosphere, the radioisotope of C—14 is produced continuously as nitrogen atoms capture cosmic-ray neutrons.

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

The carbon nucleus is unstable and decays to form N-14 through β-emission.

$$^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}e \cdot t_{1/2} = 5760 \text{ year}$$

The carbon—14 nuclei react with oxygen forming $^{14}CO_2$ which get well mixed with the normal CO_2 content of the air.

Since cosmic rays are constantly impinging upon our atmosphere, the rate of production of carbon-14 and the rate of its disintegration remain at equilibrium (steady-state). This means that its concentration has remained constant in our atmosphere over millions of years.

Carbon dioxide is removed from the atmosphere by photosynthesis. A quite constant ratio of the two isotopes of carbon (C-12 and C-14) exists in the CO_2 of the air, and this same ratio continues into plants and animal life. This has been possible because both

plants and animals excrete consumed C-14, *etc.* so that the ratio of the two isotopes remains constant during the lifetime of the plant or animal.

After death the plant no longer participates in photosynthesis and thus no longer consumes $^{14}CO_2$. Other organisms that consume plants for food also stop consuming $^{14}CO_2$ at death. Thus the carbon-14 continues decaying in the organism and is not replaced, so that $^{14}_{6}C/^{12}_{6}C$ ratio begins to drop. $^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}e$. By measuring the radioactivity, which remains in a given carbonaceous specimen, the age since its death can be determined. The technique of radio-carbon dating was developed by Willard F. Libby, for which he was awarded Nobel Prize. This method can now be used by the geologists, archeologists and, historians to trace events which took place thousands of years ago. The half-life of C-14 is 5760 years. With electronic counting equipment, it is possible to measure through several half-life times. Fossil materials may be dated to about 50,000 years ago.

2. Age of Minerals and Rocks. Archaelogists and geologists need to be able to estimate the age of objects that are extremely old. In these applications, use is made of the known and constant rate of decay of radioactive isotopes. For example, the age of rocks containing uranium can be estimated by measuring the ratio of U-238 to Pb-206 as the natural uranium-238 ends with the production of stable lead-206 All the lead-206 in such minerals is assumed to have come from U-238. Using a $^{238}U/^{206}Pb$ ratio of 1 to 0 as relating to the ratio at zero time and a $^{238}U/^{206}Pb$ ratio of 1 to 1 as relating to the ratio after one half-life ; *i.e.*, 4.5×10^9 year it has been found possible to approximate the age of these rocks.

The oldest object (a meteorite) that have been found on earth have an age of 4.6×10^9 years using this method. The life of other rocks that do not contain uranium and objects other than rocks can be estimated by using potassium argon method. K-40 is present in living organisms It decays by electron capture to argan-40 with a half-life of 1.3×10^9 years.

$$^{40}_{19}K + ^{0}_{-1}e \longrightarrow ^{40}_{18}Ar \qquad t_{1/2} = 1.3 \times 10^9 \text{ yr}$$

In determining the age of rocks, *etc.*, the ratio of ^{40}K to ^{40}Ar is measured. This method can be used to date objects upto 1 million years old, because of the longer half-life of K-40.

Thus from the measured specific activity of an object an estimate of the age of the object can be made from the equations,

$$\lambda=\frac{2.303}{t}\log\frac{N_0}{N}$$

$$\lambda=\frac{0.693}{t_{1/2}}$$

and activity, $A=\lambda N$

also $A_0=\lambda N_0$

Thus, $\frac{A_0}{A}=\frac{N_0}{N}$

Exercise 13.7. The decay rate of an object is 10 disintegrations $min^{-1}\ g^{-1}$ of carbon. Calculate the age of the object. Half-life of ${}^{14}_{6}C$ is 5,760 years. Fresh simple of ${}^{14}_{6}C$ disintegrates at the rate of 15 $min^{-1}\ g^{-1}$.

Solution. Half-life period of ${}^{14}_{6}C$ is 5,760 yr. According to equation,

$$\lambda=\frac{0.693}{5760\text{ yr}}=1.20\times10^{-4}\text{ yr}^{-1}$$

Now A_0 (activity of ${}^{14}_{6}C$ in fresh sample)$=15$

A (activity of ${}^{14}_{6}C$ in an object)$=10$

Now from the equation

$$\lambda=\frac{2.303}{t}\log\frac{A_0}{A}$$

$$t=\frac{2.303\times5760}{0.693}\log\left(\frac{15}{10}\right)$$

$$t=3.371\text{ yr}$$

Exercise 13.8. A piece of a wood found in Nalanda excavation has 40% as much ${}^{14}_{6}C$ as ordinary wood has at present. When did this get buried? Assume the half-life of ${}^{14}_{6}C$ to be 5,760 years.

Solution. We know that

$$\lambda=\frac{0.693}{t_{1/2}}=\frac{0.693}{5760}\,yr^{-1}$$

Also $$\frac{A_0}{A}=\frac{100}{40}$$

Putting these values in the expression

$$t=\frac{2.303}{\lambda}\log\frac{A_0}{A}$$

$$t=\frac{2.303\times 5760}{0.693}\log\frac{100}{40}\,yr$$

$$t=7,617\ yr$$

3. **Medical uses of radio nuclides**

(*i*) Radiation may be used to destroy malignant cells and thereby prevent the spread of cancer. Penetrating γ-radiation from cobalt-60 is used to irradiate cancer patients.

(*ii*) In medicine, radioactive isotopes can be used as **tracers** for diagnostic purposes. A tracer is a very small amount of a radioisotope added to a large amount of non-radioactive isotopes of elements. A radiation detector can be used to follow the path of the element through out the body.

Salt solutions containing ^{24}Na is injected into the bloodstream in order to follow the flow of blood and locate obstructtions in the circulatory system.

Iodine-131 concentrates in the thyroid gland, the liver, and certain parts of the brain, and is used to monitor goitre and other thyroid problems, as well as liver and brain tumors.

(*iii*) Radiations are used in the sterilization of surgical instruments.

4. **Agricultural uses of radionuclides.** Labelled samples of fertilizers are used to investigate the nutrient uptake by plants and to study the growth of crops.

Radiation experiments performed on ungerminated seeds have been helpful in increasing yield of better crops. Radiations are being used for developing high yielding varieties of rice, wheat, groundnut, jute, *etc*.

Food spoilage has been reduced by irradiation. Neutron and gamma radiation are effective for the preservation (through sterilization) of foodstuffs like fruits, potatoes. onions, fish, *etc*. Radiations are helpful for disinfecting food grains.

5. Other applications. Radioactive tracers are also used in industries to find the wear and tear in the machines, thickness of the materials, in monitoring the packing line, leakage in pipe, *etc.* They are also and in checking the contaminants.

Irradiation of polymers can lead to the formation of more cross-links between the polymer chains, so producing a more rigid structure.

There are many examples of analytical uses of radioactive isotopes. One of these techniques, called neutron activation analysis involves the bombardment of non-radioactive isotopes with neutron in a nuclear reactor. As a result, a neutron rich and radioactive in nature nucleus is produced. The radioactive species will have a characteristic half-life and the presence of the element can be detected. The concentration of the elements in a sample can be determined from the intensity of the radioactivity produced. Another technique, called isotope dilution, is used in effecting impossible separation of a desird substance.

Chemical Investigations

Radioactive isotopes find uses in the following chemical investigations :

(*i*) In elucidating structure of the chemical compounds.
(*ii*) In studying reaction mechanism.
(*iii*) In studying reaction rates.
(*iv*) In studying mechanism and action of catalysts.
(*v*) In estimating the amounts of certain chemical species.

13.10 1. Radiation and Human Health

Radioisotopes are useful to mankind both directly and indirectly. Radiations may be harmful to man and other living organisms. The high energies of alpha, beta and gamma radiations ionize molecules within tissue and cells and the chemical changes resulting from the ionization formation (on ionization formation of free radicals, H_3O^+ ions and some other species takes place that initiate chemical changes) can harm the biochemistry of a cell, and ultimately destroy an entire organ or lead to death. The effect on genetic material (DNA) can be particularly harmful because it leads to mutations that can be passed on to future generations.

Exposure to radiation causes other biological changes besides cell death. Mortality rates increase. Apparent changes in the density of fine blood vessels, the formation of eye cataracts and even the graying of hair are caused by high energy radiations. They also reduce the effectiveness of enzymes, or even damage chromosomes. Thus, it is necessary to he very careful with these radiations.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions :

13.1. **Choose the correct answer of the four alternatives given for the following questions :**

(*i*) Atom bomb is based on

(*a*) nuclear fusion (*b*) nuclear fission
(*c*) induced radioactivity (*d*) disintegration.

(*ii*) When ${}^{238}_{92}U$ decays, it emits an α particle, the new nuclide in turn emits a β particle producing another new nuclide which also decays giving a β particle and yet another new nuclide 'X'.
The mass number and the atomic number of 'X' are respectively :

(*a*) 234 and 92 (*b*) 234 and 90
(*c*) 232 and 88 (*d*) 234 and 88.

(*iii*) A radioisotope has a half-life of 12.5 years. What percentage of the original would you expect to remain after 100 years ?

( ) 0.394, (*b*) 12.5,
(*c*) 6.25, (*d*) 8.

(*iv*) Which of the following projectiles is the best for bombarding the nuclides ?

(*a*) α particle, (*b*) proton,
(*c*) deuteron, (*d*) neutron.

(*v*) Which of the following has the maximum penetrating power ?

(*a*) α-rays, (*b*) β-rays,
(*c*) γ-radiations (*d*) positrons.

(*vi*) Neptunium ${}^{239}_{94}Np$ is a radioactive element and emits β particle giving :

(*a*) ${}^{239}_{92}U$ (*b*) ${}^{234}_{88}Ra$

(*c*) ${}^{239}_{94}Pu$ (*d*) ${}^{234}_{90}Th$

(*vii*) Which of the following nuclear changes is incorrect ?

(*a*) ${}^{40}_{20}Ca + {}^{1}_{0}n \rightarrow {}^{40}_{19}K + {}^{1}_{1}H$

(*b*) ${}^{24}_{12}Mg + x \rightarrow + {}^{27}_{14}Si + {}^{1}_{0}n$

(*c*) ${}^{113}_{48}Cd + {}^{1}_{0}n \rightarrow {}^{114}_{48}Cd + {}^{0}_{-1}e$

(*d*) ${}^{42}_{29}Co + \alpha \rightarrow {}^{46}_{21}Sc + {}^{2}_{1}H$

(*viii*) In a nuclear reactor, the moderator serves to
- (*a*) absorb neutrons.
- (*b*) absorb the energy released.
- (*c*) accelerate the neutrons.
- (*d*) control the speed and number of neutrons.

(*ix*) Which of the following particles is emitted in the nuclear reaction ?

$$^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow {}^{30}_{15}\text{P} + \ldots ?$$

- (*a*) $^{1}_{0}\text{n}$
- (*b*) $^{0}_{-1}\text{e}$
- (*c*) $^{1}_{1}\text{H}$
- (*d*) $^{2}_{1}\text{H}$

(*x*) The phenomenon of radioactivity is associated with :
- (*a*) decay of nucleus.
- (*b*) fusion with nucleus.
- (*c*) emission of electrons or protons.
- (*d*) rearrangement in the extranuclear electrons.

13.2. Fill in the blanks :

(*i*) The.........particle has the same mass and charge as a helium nucleus, whereas the...........particle is essentially a high speed electron that has been ejected from the nucleus of an atom of a ....element.

(*ii*) Radioactivity of a nuclide is measured in terms of.........period.

(*iii*) The conversion of one element into another element by using a suitable projectile is called.........

(*iv*) When an isotope undergoes α-decay, its proton number decreases by.........and its nucleon number decreases by.........

(*v*) In a.........reaction, a rearrangement of the.........and.........in the nucleus of the atom takes place.

(*vi*) Marie Curie succeeded in isolating compounds of two new elements from the uranium ore.........

(*vii*) A nuclear reaction which produces greater energy than uranium fission is the.........of two.........nuclei.

(*viii*) A change in a gene of a cell, on exposure to radiations, that is then passed on to the other cells is called a.........

(*ix*) The spontaneous.........of atoms is responsible for radioactivity and those isotopes which decay in this way are said to be.........

(*x*) ....particle is ejected when a neutron is converted to a proton and an electron.

13.3. Which of the following statements are true (T) or false (F) :

(*i*) The total number of nucleons in a nucleus is equal to the total number of protons and neutrons in the nucleus.

(*ii*) On β-emission the mass number decreases by four units and the atomic number decreases by two units.

(*iii*) In α-decay there is no change in mass number.

(*iv*) The energy available from the fusion of one gram of a light element is higher than from the fission of one gram of a heavy element.

(*v*) Radioactivity is an inherent property of an isotope which is not affected by temperature or pressure.

(*vi*) Alpha and beta radiations are high speed particles ejected from the nuclei of radioactive atoms.

(*vii*) Radiation is one of a number of things that might cause cancer.

(*viii*) The sun obtains its energy from the fusion of hydrogen atoms.

(*ix*) Carbon-14 dating can be used to calculate the age of plant and animal remains.

(*x*) Uranium-238 undergoes nuclear fission.

SHORT ANSWER QUESTIONS

13.4. How does artificial transmutation differ from artificial radioactivity ?

13.5. Complete the following reactions :

(*i*) $^{27}_{13}Al + ^{1}_{0}n \longrightarrow ^{24}_{11}Na + \ldots\ldots$

(*ii*) $^{11}_{5}B + ^{1}_{0}n \longrightarrow \ldots\ldots + ^{1}_{1}H$

(*iii*) $^{24}_{12}Mg + ^{1}_{1}H \longrightarrow ^{21}_{11}Na + \ldots\ldots$

(*vi*) $^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + \ldots\ldots$

(*v*) $^{14}_{7}N + \ldots \longrightarrow ^{17}_{8}O + ^{1}_{1}H$

(*vi*) $^{9}_{4}Be + ^{1}_{0}n \longrightarrow \ldots\ldots$

(*vii*) $^{40}_{18}Ar \longrightarrow ^{40}_{19}K + \ldots\ldots$

(*viii*) $^{32}_{16}S + \ldots \longrightarrow ^{32}_{15}P$

(*ix*) $\ldots\ldots + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$

(*x*) $^{23}_{11}Na + ^{1}_{0}n \longrightarrow \ldots\ldots + \gamma$

(*xi*) $^{63}_{29}Cu + ^{1}_{1}H \longrightarrow \ldots\ldots\ ^{1}_{0}n$

(*xii*) $^{109}_{47}Ag + ^{1}_{0}n \longrightarrow \ldots\ldots\ \gamma$

13.6. Write nuclear equations for the following processes :

(*i*) $^{27}_{13}\text{Al}\ (\alpha, n)\ ^{30}_{15}\text{P}$

(*ii*) $^{209}_{83}\text{Bi}\ (d, n)\ ^{210}_{84}\text{Po}$

(*iii*) $^{15}_{7}\text{N}\ (p, \alpha)\ ^{12}_{6}\text{C}$

(*iv*) $^{12}_{6}\text{C}\ (p, \gamma)\ ^{13}_{7}\text{N}$

(*v*) $^{59}_{27}\text{Co}\ (n, \gamma)\ ^{60}_{27}\text{Co}$

(*vi*) $^{31}_{15}\text{P}\ (d, p)\ ^{32}_{15}\text{P}$

13.7. (*i*) What disadvantages do protons and α particles have as nuclear projectiles ?

(*ii*) What advantages do protons have over α particles as nuclear projectiles ?

(*iii*) Why are neutrons superior to protons and α particles as nuclear projectiles ?

13.8. (*i*) The half-life of plutonium -214 is 1.5×10^{-4} seconds. How much of plutonium will be left after 3×10^{-4} seconds, and 1.5×10^{-3} seconds from 3 g of plutonium ?

(*ii*) The half life of cobalt-60 is 5.3 years. Starting with 10.0 mg of Co-60, how much will remain after 21.2 years ?

(*iii*) The fission reaction

$$^{235}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{92}_{36}\text{Kr} + ^{141}_{56}\text{Ba} + 3\,^{1}_{0}\text{n}$$

is reported to release 175 MeV of energy per nucleus fissioned. Calculate the quantity of energy (in kJ) released by the fission of one gram of U-235.

TERMINAL QUESTIONS

13.1. What are the kinds of naturally occurring radioactive decay ? How do they differ from each other ?

13.2. What is a radioactive decay series ? For ^{238}U, why does it stop at ^{206}Pb ?

13.3. Describe the process of electron capture. How can this process be detected ?

13.4. What is the belt of stability ? What decay processes are likely to occur for nuclides that have n/p ratios that place them above the band of stability ?

13.5. What are the types of radiations given off by radioactive substances ? How does the emission of each one of them affect the nucleus undergoing change ? What is the law governing the rate of radioactive change ?

13.6. (*a*) Define and explain the term 'half-life period'.

(*b*) What is radioactive constant ? How is the constant related to half-life period ?

13.7. (*a*) Give a brief account of various types of nuclear reactions.

(*b*) Write the name associated with the following symbols :

(i) $^{4}_{2}He$, (ii) $^{0}_{-1}e$,

(iii) $^{0}_{+1}e$, (iv) $t_{1/2}$,

(v) $^{2}_{1}H$, (vi) $^{1}_{0}n$.

13.8. Give a brief account of radioactivity. How does it differ from artificial radioactivity? Define and illustrate artificial transmutation.

13.9. Define and explain binding energy. Calculate the mean binding energy for the helium nucleus.

13.10. (a) Why are α-particles deflected less than β particles in an electric field?

(b) What is the difference between

(i) Fission and fusion.

(ii) A nucleon and a neutron.

(iii) A β particle and an electron.

(iv) A α particle and helium atom.

13.11. (a) Write nuclear reactions for α-decay from

(i) Bi—210, (ii) Rn—222,

(iii) Tl—194, and (iv) Th—232.

(b) Write nuclear reactions for β-decay of

(i) Sr—90, (ii) S—25,

(iii) Co—60, and (iv) C—14.

(c) What product is formed when $^{232}_{90}Th$ decays with the stepwise loss of the following particles : α, β, β, α, α, β ? Write the equations for each step.

13.12. (a) How did the discovery of radioactivity change atomic theory?

(b) Why are neutrons considered more efficient bombarding agents than protons and α particles?

(c) Since electrons are not in the nucleus, how is it possible for electrons to be emitted in some radioactive changes?

13.13. (a) What conservation laws apply to nuclear reactions?

(b) What is a chain reaction?

(c) How can a chain reaction be initiated from the thermal-neutron-induced fission of $^{235}_{92}U$, but not with other particles?

(d) Why do fission chain reactions not occur in natural uranium ores?

13.14. (a) What type of objects can be dated by means of radiocarbon dating?

(b) Outline the importance or uses of the following isotopes :

$^{60}_{27}Co$, $^{131}_{54}I$, $^{32}_{15}P$ and $^{239}_{94}Pu$

(c) What chemical reactions usually occur once α, β, or γ-radiation has been ingested into the body?

(d) Why is biological damage from γ-radiation likely to be dangerous?

(*e*) When is body exposure to α-radiation thought dangerous to one's health ?

(*f*) Describe four practical applications of radioactivity.

13.15. (*a*) Balance the following equations :

(*i*) $^{60}_{28}\text{Ni} + ^{1}_{0}\text{n} \rightarrow ^{60}_{27}\text{Co} + \ldots$

(*ii*) $^{35}_{16}\text{S} \rightarrow \ldots + ^{0}_{-1}\text{e}$

(*iii*) $^{31}_{15}\text{P} + \ldots \rightarrow ^{35}_{17}\text{Cl} + ^{1}_{0}\text{n}$

(*iv*) $^{27}_{13}\text{Al} + \ldots \rightarrow ^{30}_{15}\text{P} + ^{1}_{1}\text{H}$

(*v*) $^{80}_{35}\text{Br} \rightarrow \ldots + \beta^{-}$

(*b*) Supply the nucleus or particle/particles which completes each of the following equations :

(*i*) $^{235}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{139}_{56}\text{Ba} + \ldots + 2\,^{1}_{0}\text{n}$

(*ii*) $^{239}_{94}\text{Pu} + ^{1}_{0}\text{n} \rightarrow ^{115}_{48}\text{Cd} + \ldots + 3\,^{1}_{0}\text{n}$

(*iii*) $^{235}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{90}_{38}\text{Sr} + \ldots + 3\,^{1}_{0}\text{n}$

(*iv*) $^{235}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{141}_{56}\text{Ba} + ^{92}_{36}\text{Kr} + \ldots$

13.16. (*a*) How do the atomic number and the mass number of an isotope change when its nucleus loses

(*i*) an alpha particle,

(*ii*) a beta particle,

(*iii*) gamma radiation, and

(*iv*) a neutron ?

13.17. (*a*) Half-lives for radioactive decay reactions are found to be independent of the size of the sample. What does this tell you about the kinetics of these reactions ?

(*b*) All things being equal which process produces more energy per gram of matter : fusion or fission.

13.18. What are synthetic elements ? Comment on the discovery of elements with atomic numbers, 43, 61, 85, 87. Give a few nuclear reactions for preparing transuranic elements.

13.19. (*a*) What are the transuranium elements ? Where do they occur naturally ?

(*b*) What is a nuclear transformation ?

13.20. (*a*) Define nuclear fission ? Why is it possible to have a nuclear explosion of U-235 ?

13.21. (*a*) Why does not a nucleus explode ?
(*b*) How does a nuclear reactor differ from breeder reactor ?

13.22. The isotope of $^{138}_{55}Cs$ decays through β-emission with a half-life of 32.2 minutes.

(*i*) Name the product of decay.

(*ii*) Is $^{138}_{55}Cs$ more or less stable than an isotope whose half-life is 28.7 min ?

(*iii*) What time will it take for 87.5% of a sample of pure $^{138}_{55}Cs$ to decay ?

(Ans. 1 hr 36.6 min)

(*iv*) What amount of a sample of pure $^{138}_{55}Cs$ will remain intact after 4 hour 17·6 minutes ? (Ans. 0.39%)

13.23. How much radium will be left after 845 yr from 3 g of radium ? Radium has a half-life of 1690 yr. (Ans. 2.2 g)

13.24. One g of $^{99}_{42}Mo$ decays by β-emission to 0.125 g in 200 hours. How much more time will elapse until only 0.1 g of it is left ?

(Ans. 21.45 hr)

13.25 A radioactive sample of $^{90}_{38}Sr$ had an activity of 0.250 m curie.

(*i*) Calculate the specific activity of the sample.
(*ii*) What will be the activity of the sample after 30 yr ?

Half-life period of $^{90}_{38}Sr$ is 19.9 yr.

[Ans. (*i*) 3.7×10^{13} dis g^{-1} s^{-1}
(*ii*) 6.55×10^{6} dis s^{-1}]

13.26. A sample of $^{60}_{27}Co$ decays at the rate of 240 atoms min^{-1}. Calculate the number of atoms of $^{60}_{27}Co$ in the sample. Half-life period of $^{60}_{27}Co$ is 5.2 yr. (Ans. 9.6×10^{8} atoms)

13.27. Calculate the age in the following cases :

(*a*) A piece of hair has 30% as much $^{14}_{6}C$ as it has today. Half-life period of $^{14}_{6}C$ is 5600 yr. (Ans. 9727 yr)

(*b*) The bones of an animal had ${}^{14}_{6}C$ activity of 2.8 dis min^{-1} g^{-1} of carbon. The specific activity of ${}^{14}_{6}C$ is 15.3 dis min^{-1} g^{-1}. Half-life for ${}^{14}_{6}C$ is 5670 yr. **(Ans. 14000 yr)**

ANSWERS TO SELF ASSESSMENT QUESTIONS

13.1. (*i*) (*b*) (*ii*) (*a*) (*iii*) (*a*) (*iv*) (*d*) (*v*) (*c*)
(*vi*) (*c*) (*vii*) (*c*) (*viii*) (*d*) (*ix*) (*a*) (*x*) (*a*)

13·2. (*i*) alpha, beta, radioactive,
(*ii*) half-life,
(*iii*) transmutation,
(*iv*) 2, 4,
(*v*) nuclear, protons, neutrons,
(*vi*) pitchblende,
(*vii*) fusion, hydrogen,
(*viii*) mutation,
(*ix*) disintegration, radioactive,
(*x*) beta.

13.3. (*i*) T (*ii*) F (*iii*) F (*iv*) T
(*v*) T (*vi*) T (*vii*) T (*viii*) T
(*ix*) T (*x*) F

13.4. Artificial radioactivity pertains to the decay of the product obtained when a stable nuclide is bombarded with some fast moving particle, *e.g.*,

$${}^{27}_{13}Al + {}^{4}_{2}He \longrightarrow \underset{\text{(Radioactive)}}{{}^{30}_{15}P} + {}^{1}_{0}n$$

$${}^{30}_{15}P \longrightarrow {}^{30}_{14}Si + {}^{0}_{1}e$$

In artificial transmutation, the product obtained by bombarding with high speed particles does not decay further, *e.g.*,

$${}^{14}_{7}N + {}^{4}_{2}He \longrightarrow \underset{\text{(Stable nuclide)}}{{}^{17}_{8}O} + {}^{1}_{1}H$$

13.5. (*i*) ${}^{27}_{13}Al + {}^{1}_{0}n \longrightarrow {}^{24}_{11}Na + {}^{4}_{2}He$

(*ii*) ${}^{11}_{5}B + {}^{1}_{0}n \longrightarrow {}^{11}_{4}Be + {}^{1}_{1}H$

(*iii*) ${}^{24}_{12}Mg + {}^{1}_{1}H \longrightarrow {}^{21}_{11}Na + {}^{4}_{2}He$

(iv) $^{9}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He} \longrightarrow ^{12}_{6}\mathrm{C} + ^{1}_{0}\mathrm{n}$

(v) $^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \longrightarrow ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H}$

(vi) $^{9}_{4}\mathrm{Be} + ^{1}_{0}\mathrm{n} \longrightarrow ^{10}_{4}\mathrm{Be} + \gamma$

(vii) $^{40}_{18}\mathrm{Ar} \longrightarrow ^{40}_{19}\mathrm{K} + ^{0}_{-1}\mathrm{e}$

(viii) $^{32}_{16}\mathrm{S} + ^{0}_{-1}\mathrm{e} \longrightarrow ^{32}_{15}\mathrm{P}$

(ix) $^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \longrightarrow ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H}$

(x) $^{23}_{11}\mathrm{Na} + ^{1}_{0}\mathrm{n} \longrightarrow ^{24}_{11}\mathrm{Na} + \gamma$

(xi) $^{63}_{29}\mathrm{Cu} + ^{1}_{1}\mathrm{H} \longrightarrow ^{63}_{30}\mathrm{Zn} + ^{1}_{0}\mathrm{n}$

(xii) $^{109}_{47}\mathrm{Ag} + ^{1}_{0}\mathrm{n} \longrightarrow ^{110}_{47}\mathrm{Ag} + \gamma$

13.6. (i) $^{27}_{13}\mathrm{Al} + ^{4}_{2}\mathrm{He} \longrightarrow ^{30}_{15}\mathrm{P} + ^{1}_{0}\mathrm{n}$

(ii) $^{209}_{83}\mathrm{Bi} + ^{2}_{1}\mathrm{H} \longrightarrow ^{210}_{84}\mathrm{Po} + ^{1}_{0}\mathrm{n}$

(iii) $^{15}_{7}\mathrm{N} + ^{1}_{1}\mathrm{H} \longrightarrow ^{12}_{6}\mathrm{C} + ^{4}_{2}\mathrm{He}$

(iv) $^{12}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H} \longrightarrow ^{13}_{7}\mathrm{N} + \gamma$

(v) $^{59}_{27}\mathrm{Co} + ^{1}_{0}\mathrm{n} \longrightarrow ^{60}_{27}\mathrm{Co} + \gamma$

(vi) $^{31}_{15}\mathrm{P} + ^{2}_{1}\mathrm{H} \longrightarrow ^{32}_{15}\mathrm{P} + ^{1}_{1}\mathrm{H}$

13.7. (i) Both protons and α particles are positively charged particles. They will be repelled by the positive nucleus of any target atom they approach.

(ii) Both protons and α particles are positively charged particles. Protons can be accelerated to greater speed than α particles as they are lighter particles.

(iii) Neutrons are neutral particles whereas protons and α particles are positively charged particles. Neutrons are not repelled by the positive nucleus of any target, they approach.

13.8. (*i*) Starting with 3 g of plutonium, only 1.5 g will be left after 1.5×10^{-4} seconds. After 3×10^{-4} seconds, the 1.5 g would have decayed to 0.75 g and after 1.5×10^{-3} seconds only $\frac{3}{1024}$ g would remain (ten half-lives).

(*ii*) The number of half lives in 21.2 years.

$$= \frac{21.2}{5.3} = 4 \text{ half-lives.}$$

Amount of Co-60 would remain after 21.2 years.

$$= \frac{10}{2 \times 2 \times 2 \times 2} = 0.625 \text{ mg.}$$

(*iii*) Energy released per nucleus fissioned = 175 Mev.

Molar mass of U-235 = 235 g/mol

Number of nuclei per mole = 6.02×10^{23}

i.e., 235 g U-235 give 6.02×10^{23} nuclei.

Total energy released = $6.02 \times 10^{23} \times 175$ Mev

Energy released from 1 g uranium-235

$$= \frac{6.02 \times 10^{23}}{235} \times 175 \text{ Mev}$$

$$= \frac{6.02 \times 10^{23} \times 175 \times 1.6 \times 10^{-13}}{235} \text{ Joules}$$

$$= 7.71 \times 10^{10} \text{ J} \qquad (\because 1 \text{ Mev} = 1.6 \times 10^{-13} \text{ Joules})$$

$$= 7.71 \times 10^{7} \text{ kJ}$$

□ □

UNIT 14

Surfaces and Catalysis

When matter is finally divided, its suface is enormously increased and its properties undergo a variety of changes. The increased fraction of molecules present at or near the surface and the unbalanced distribution of the matter about them impart new characteristics to the surface.

UNIT PREVIEW

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Explain the phenomenon of adsorption.
2. Differentiate between adsorption and absorption ; adsorbent and adsorbate.
3. Comment on the chemical and physical adsorption.
4. State the factors which help the process of adsorption.
5. Understand the adsorption of gases on solids the factors which govern it.
6. Comment on the adorption of solutes from solutions by solids.
7. Describe the nature of the colloidal state.
8. State the distinctions between true solutions and colloidal suspensions.
9. List the characteristics of colloids.
10. Comment on the various systems of classifications of colloidal dispersions.
11. Describe micelles and emulsions.
12. Describe methods of preparation and purification of colloidal dispersions.
13. Describe the various properties of colloidal dispersions.

14. Understand the terms : lyophobic and lyophilic colloids, peptization, electrophoresis, gold number, dialysis, and other terms appearing in the unit.
15. Explain how catalysts act to lower the energy requirements of a reaction.
16. Describe the nature of homogeneous and heterogeneous catalysts.
17. Comment on the nature of solid catalysts and shape-selective catalysis.

14.1. INTRODUCTION

Surface chemistry is that branch of chemistry which deals with the reactions occuring at the large area of surface of particles (colloidal particles, ions, atoms or molecules). A chunk of matter may be composed of like atoms throughout, yet these atoms at its surcace, edges and corners are different from those within the bulk of the matter because they are not fully surrounded by other similar atoms. Thus, atoms at the surface of the matter are not fully satisfied with valence bonds. As a result, all such atoms react at the first instance, with other types of atoms and molecules in the proximity of the surface. On the basis of size of the particles involved in such reactions, surface chemitry may be subdivided in two general area which essentially are governed by common principles.

The first involves the study of reactions on the surface of the particles (solid catalysts). Molecules in the gas or the liquid phase can adhere to solid surfaces and this phenomenon is referred to as **adsorption**. Adsorption of molecules on the surface of catalysts is vital in many reactions. The second pertains to the study of reactions on the surface of the particles which fall in the region of colloidal state. It is not a homogeneous state. Material like starch in the powdered form wheh heated with water give a heterogeneous mixture ; the particles of insoluble starch do not settle but remain suspended. Such a state is referred to as **colloidal state**.

Rough surface and finely divided materials display pronounced surface effects. In this unit we shall discuss adsorption phenomenon, colloidal state of substances and about catalysis.

14.2. ADSORPTION

Surfaces of both liquids and solids, unlike their bulk are constantly under the influence of unbalanced attractive forces. These unbalanced forces are called residual valence forces. Solids in particular are endowed with unbalanced forces at their surfaces by the incomplete valence bonds.

As a result, solid surfaces tend to satisfy their residual forces by attracting and retaining on them the molecules of other substances which come in their contact. As the molecules remain only at the surface and do not pentrate into the bulk, their concentration is more at the surface than in the bulk of the solid. The

phenomenon of higher concentration of any substances on the surface than in the bulk of a solid is called **adsorption** (Fig. 14.1.) Thus adsorption refers to the relatively higher concentration of the adsorbed material on the surface of the adsorbent (solid) as compared to its concentration in the bulk phase (of the absorbed material).

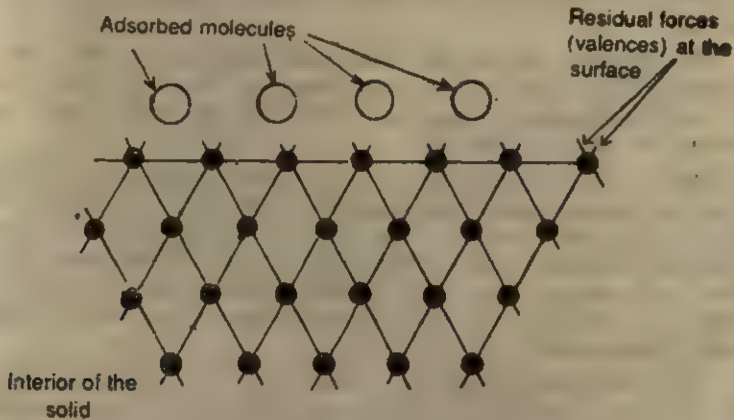


Fig. 14.1. Adsorption on the surface of a solid by residual forces (valences).

Adsorption, on the other hand, is applied to a more or less uniform distribution of one in the other. In practice, however, it is difficult to separate the effects of the two, particularly for systems of gases and solids. Thus, water vapour is absorbed by anhydrous

Fig. 14.2. Absorption and adsorption. Solid A has absorbed the gas uniformly. Solid B has adsorbed the gas at its surface.

calcium chloride while it is adsorbed by silica gel. Similarly, while ammonia is absorbed in water, it is adsorbed by charcoal. The difference between absorption and adsorption is portrayed in Fig. 14.2.

Adsorption is a fast process as compared to absorption which is a slow process because it involves the diffusion into the interior of the matter.

The material upon whose surface the adsorption of some substances takes place is said to be **adsorbent** and the substance adsorbed is called **adsorbate** (adsorbed phase). The removal of adsorbed substance is called **desorption**.

The process of adsorption is associated with evolution of energy, and hence, exothermic in nature. The heat change in a specific adsorption process of one mole of adsorbate on an adsorbent surface is termed an **enthalpy** or **heat of adsorption**. As a result of adsorption, the residual valence forces of the adsorbent and consequently its energy of adsorption decreases. The energy is lost as heat of adsorption.

These forces can further be created by breaking the solid (Fig. 14.3) or by extending its crystal lattice. On breaking the solid, the interior forces holding the molecules together within the body of a solid become free which attract particles of gases and solutions around. Thus, increase in surface area and unbalanced forces increase adsorption.

Fig. 14.3. A simple representation of increase in surface area and unbalanced forces.

14.2.1. Types of Adsorption

The forces involved in adsorption are of various types such as van der Waals forces and even chemical bond forces.

If the adsorbate is held on the surface of the adsorbent by van der Waals forces, the adsorption is called **physical adsorption**. If the forces are nearly as strong as chemical binding forces, the adsorption is named **chemisorption**. (or activated adsorption or Langmuir adsorption).

We know, adsorption is an exothermic process and occurs with a decrease in enthalpy. For chemisorption, enthalpy decrease is two to ten times greater than that for van der Waals adsorption. A comparison between these two types of adsorption is given in Table 14.1.

TABLE 14.1. Comparison of physical and chemical adsorptions

Physical adsorption	*Chemical adsorption*
1. It is not very specific.	1. It is highly specific.
2. Heat of adsorption is relatively small, *i.e.*, about 20-40 kJ mol^{-1}.	2. Heat of adsorption is relatively large, *i.e.* about 40-400 kJ mol^{-1}.
3. General occurs at low temperature and decreases with rise in temperature.	3. Usually occurs at high temperatures.
4. Equilibrium is attained rapidly. It is reversible as molecules are not strongly retained by adsorbent.	4. Equilibrium is attained slowly. It is irreversible as the molecules are strongly retained by adsorbent.
5. Rate of adsorption increases with increase of presure of adsorbate. Near saturation pressure multilyers are formed.	5. Rate of adsorption usually increases with increase of pressure of adsorbate. Near saturation pressure adsorption rate decreases. Adsorption is confined only to monolayer.
6. Depends on the nature of adsorbate. Degree of adsorption is high for more easily liquefiable and soluble [illegible]	6. There appears to be no correlation Degree of adsorption depends on the chemical properties of both adsorbate and adsorbent. Gases capable of forming compounds wrth adsorbent are adsorbed in higher proportions.
7. Activation energy does not appear to effect the reaction.	7. Reactions appear to be activated by activation energy involved in reactions.
8. Depends on the surface of adsorbent.	8. Depends on the surface of adsorbent.

14.3. ADSORPTION OF GASES ON SOLIDS

The extent of adsorption of a gas on a solid depends upon the following factors :

(1) Nature of the gas.

(2) Nature of adsorbent and its surface area.

(3) Temperature.

(4) The partial pressure of the gas (in the gas phase).

(5) Activation state of the adsorbent.

1. **Nature of gas.** It has been seen that the more readily soluble and easily liquefiable gases such as NH_3, HCl, Cl_2 and SO_2 are adsorbed more than so called 'permanent' gases such as H_2, N_2 and O_2. This is because of the fact that the van der Waals or molecular forces which are involved in adsorption are more predominant in the former category than in the latter cases.

2. **Nature of adsorbent**. Substances with large surface area, *e.g.*, charcoal and silica gel are the common adsorbents. Charcoal, a microcrystalline form of graphite adsorbs easily liquefiable gases readily and strongly. This property has been adopted in manufacturing gas-masks for protection against poisonous gases. Zeolite, a complex silicate with porous structure, is a good adsorbent. Hydrogen is adsorbed by metals like palladium and platinum. Oxygen and nitrogen are also adsorbed by metals. Thus, the greater the surface area, the greater the adsorption. Colloidal particles are good adsorbents because they provide a large surface area for adsorption. Porous surfaces are better for adsorption. The size of the pores should be such which can allow the diffusion of gases.

3. **Effect of temperature**. The process of adsorption being exothermic in nature will not be favoured by rise in temperature (Le Chatelier's principle). Increase in temperature should thus decrease the amounts adsorbed. A graph drawn between the mass (x) of gas adsorbed by mass (m) of adsorbent (x/m) and temperature (t) at a constant pressure is called **adsorption isobar**. The adsorption isobars for physical adsorption and chemisorption are shown in Fig. 14.4.

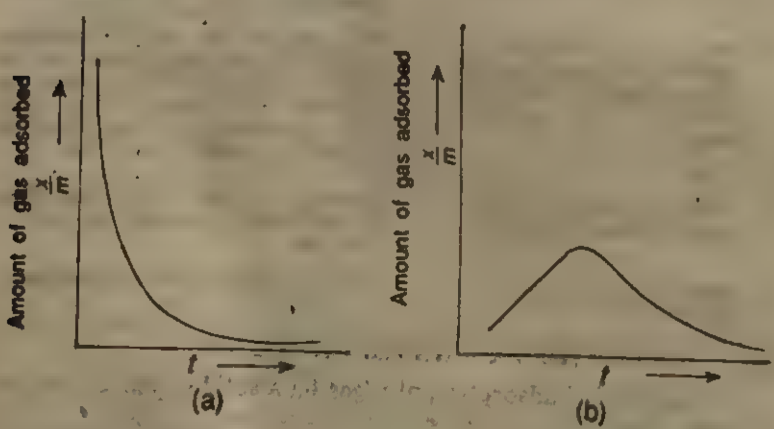


Fig. 14.4. Variation of adsorption with temperature at constant pressure : adsorption isobars ; (a) in physical adsorption ; (b) in chemical adsorption.

Physical adsorption isobar [Fig. 14.4 (*a*)] shows a regular decrease in the amount of gas adsorbed with increase in temperature.

Chemical adsorption isobar shows an initial increase in the amount of gas adsorbed with temperature and then a regular decrease as the temperature increases.

This initial increase is due to the fact that, like chemical reactions, chemisorption also requires activation energy. This fact is a proof of bonding between adsorbate and adsorbent, like chemical bonding. Thus these isobars are helpful in finding out the nature of adsorption.

4. **Effect of pressure.** The amount of gas adsorbed by an adsorbent depends upon the pressure of a gas. It follows that the increase in pressure will increase in adsorption. This increase of adsorption is, however, not directly proportional to the pressure applied as evidenced by the plot (Fig. 14.5) of amount of gas adsorbed against pressure of the gas at constant temperature. This plot is called adsorption isotherm.

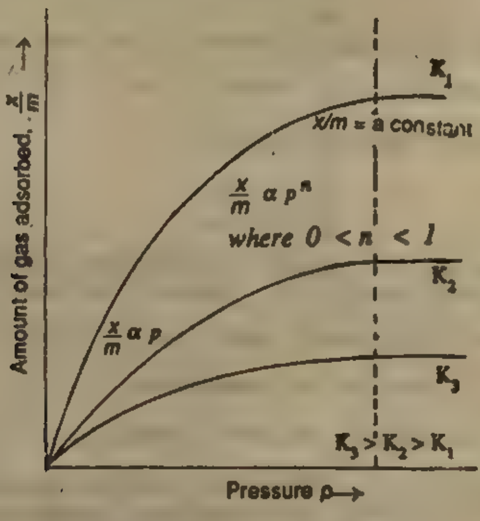


Fig. 14.5. Adsorption isotherm.

The isotherm of this type is encountered with adsorption of unimolecular layer in nature (chemisorption). In the beginning the amount of gas adsorbed for a given quantity of adsorbent increases rapidly with pressure and towards the end very slowly as the surface becomes covered with gas molecules. Later, a stage is reached when no more gas is adsorbed even if pressure is increased. This state is referred to as **saturation stage** and the pressure applied is known as **saturation pressure** (p_s).

The variation of mass of adsorbed gas per unit mass of adsorbent with pressure is often expressed by an empirical expression proposed by H. Freundlich.

$$\frac{x}{m}=kp^n \qquad ...(14.1)$$

(where n lies between 0 and 1)

where x is the amount of a gas adsorbed by mass m of the adsorbent at the pressure p, so that x/m denotes amount of the gas adsorbed per unit mass of the adsorbent. The terms n and k are constants depending upon the nature of the adsorbent, adsorbate and temperature.

The behaviour of adsorption is nicely explained by the equation (14.1) at low pressures. At low pressures, the amount adsorbed is proportional to pressure, but that a limiting constant value is approached at high pressures.

Thus, the equation (14.1) for high pressure range turns out to be,

$$\frac{x}{m}=kp^{\circ} \qquad ...(14.2)$$

At intermediate range of pressure, the amount of gas adsorbed $\left(\frac{x}{m}\right)$ is proportional to p^n, where $0 < n < 1$ or $\frac{x}{m}$ will depend upon the fractional power of pressure, *i.e.*,

$$\frac{x}{m}=kp^{\frac{1}{n}} \qquad ...(14.3)$$

Thus, the equation appears to have no theoretical basis but has been found quite useful. The constants in the equation can be determined by plotting $\log\frac{x}{m}$ versus $\log p$. So taking logarithms on both sides of equation (14.3), we obtain,

$$\log\frac{x}{m}=\log k+\frac{1}{n}\log p \qquad ...(14.4)$$

This equation is similar to an equation of straight line $y=mx+c$. Thus, a plot (Fig. 14.6) between $\log x/m$ and $\log p$ will turn out to be straight line with an intercept on the $\log\left(\frac{x}{m}\right)$ axis equal to $\log k$ and the slope of the line equal to $\frac{1}{n}$.

In general, therefore

$$\frac{x}{m}\propto p^n$$

where with increasing pressure, the value of n decreases from 1 at low pressure to zero at high pressure.

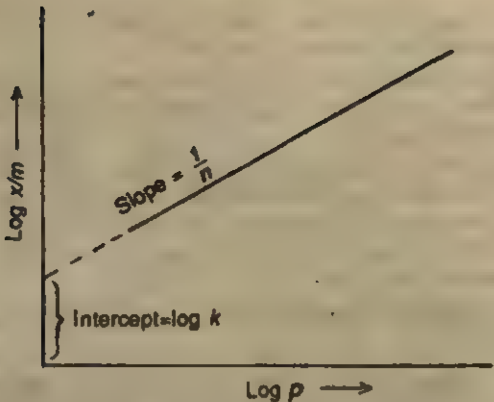


Fig. 14.6. Freundlich adsorption isotherm. A linear plot between log $\frac{x}{m}$ and log p.

Various types of adsorption isotherms with multilayer adsorption are shown in Fig. 14.7.

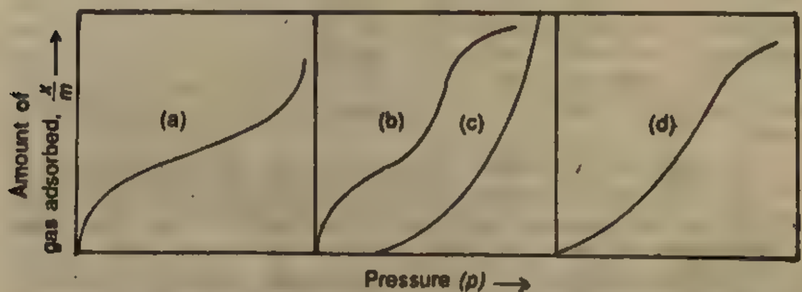


Fig. 14.7. Adsorption isotherms for physical adsorption.

5. **Effect of activated adsorbent.** Activated adsorbent is capable of adsorbing the adsorbates to a great extent. Primarily activation leads to increase in the surface area of the adsorbent which effectively helps in the adsorption process. This can be achieved in the following ways :

(*a*) **Creation of rough surface** by mechanical rubbing, chemical action or by depositing finely dispersed metals by electroplating. Generally metallic adsorbents are activated by these treatments.

(*b*) **Increase of effective surface** area by subdividing the adsorbent into smaller fine pieces or grains. Treatment with superheated steam and dilute acids have also been useful for activating the adsorbent surfaces. Generally non-metallic adsorbents are

activated by these methods. Extremely fine powder hampers the adsorption process as the pores are choked.

Valence bond forces also affect the process of chemisorption. Atoms situated at surface, edge, corner and peak have different powers for chemisorption.

The **specific surface area** of a solid (in the form of a powder or porous mass) is defined as the surface area (in square metres) per gram of the adsorbent. Highly active solids with large surface areas (several hundred square metres per gram) are used as catalysts. Such catalysts help the process of adsorption.

14.4. ADSORPTION OF SOLUTES FROM SOLUTION BY SOLIDS

Solid surfaces are capable of adsorbing certain dissolved matter from solution in preference to other solutes and solvents. Activated animal charcoal (one from which pre-adsorbed gases have been removed) can adsorb certain colouring matter present in sugar solution, and making it colourless. It also adsorbs out certain acids partly such as oxalic acid or acetic acid present in water, and thus, the concentration of acid decreases. Similarly, activated charcoal can adsorb out ammonia from solutions of aqueous ammonia phenolphthalein from solutions of acids or bases, *etc.* In the detection of Al^{3+} by 'lake test', litmus is adsorbed by gelatinous precipitate. Organic matters like charcoal tend to adsorb electrolytes more readily than non-electrolytes and inorganic solids like AgCl have preference for electrolytes (freshly precipitated AgCl tends to adsorb either Ag^+ or Cl^- ions depending upon which are in excess).

In cases referred above and others, the extent of adsorption increases with the molecular mass of the adsorbate. This preferential tendency of adsorbents leads to phenomena of **negative and positive adsorptions**. From dilute solutions of KCl, blood charcoal adsorbs water and thus, concentration of KCl is increased. This type of adsorption is known as **negative adsorption**. However, from concentrated solutions of KCl, blood charcoal adsorbs KCl, rather than water. This is known as **positive adsorption**.

The principles and factors applicable for adsorption of gases also hold good for adsorption from solutions. Increase in temperature appears to decrease the extent of adsorption whereas an increase in surface area increases it. In the process of adsorbing solutes from solution an equilibrium between the amount adsorbed on the surface and the concentration of the solute in solution is established. The way the adsorption behaves with concentration of solute is described by Freundlich's equation used for gases. Thus, the equation in terms of concentration turns out to be,

$$\frac{x}{m}=kc^{1/n}$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \quad \ldots(14.5)$$

where x, m, n and k have the same meaning, c is the equilibrium concentration of the solute.

A plot of log (x/m) against log c is found to be a straight line over small ranges of concentrations (as was stated in the case of adsorption of gases).

14.5. THE COLLOIDAL STATE

The term colloid, from the Greek words **kolla** and **eidos** which mean **glue** and **like** respectively, was first employed in 1861 by Thomas Grahm to classify substances which generally exist in an amorphous or gelatinous condition such as starch and gelatin. He observed in his classical researches on liquid diffusion that some substances would diffuse rapidly in solution and could readily pass through animal or vegetable membranes while some others did not respond readily. Thus, he made a distinction between readily diffusible substances and others which diffused slowly. Readily diffusible, *e.g.*, urea, sugar, salts, acids, bases, *etc.*, were named **crystalloids** and others, *e.g.*, gelatin, albumen, glue, silicic acid, *etc.*, were named **colloids.**

This sort of classification could not be applied strictly as some substances could be found to behave in both ways. For example, crystalline sulphur and graphite have been found to behave like colloids as well ; colloidal glue and gelatin have been found to possess crystalline structure by X-ray analysis. Soaps also provide another good example—they behave as colloids in aqueous solution, being sparingly soluble in water and as crystalloids in alcoholic solution being highly soluble.

Thus, it has been found appropriate to use the term **colloidal state** instead of colloid as the properties characterized as colloidal are not peculiar to a specific class of substances. Any given substance may be obtained in the colloidal form by some appropriate means. Synthetic polymers and proteins because of their sizes belong to colloidal substances.

14.5.1. Characteristics of the Colloidal State

A colloidal system is always heterogeneous and consists of at least two phases : the **disperse phase** (the phase constituting the colloidal particles) and the **dispersion medium** (the medium in which these colloidal particles are dispersed).

To name any system as colloidal, size of the dispersed particles is the primary criterion. The various colloidal solutions (systems) are compared with true solutions on one hand and those of suspensions on the other.

A **true solution** is a homogeneous mixture of disperse phase and dispersion medium, *e g*., sugar, table salt, *etc*., dissolve in water and constitute (one phase) true solution.

A **suspension** is a heterogeneous mixture of a disperse phase and dispersion medium *e g*., sand, powdered glass, *etc*., in water behave as suspensions. Solute particles settle at the bottom due to their large size.

Some properties distinguishing between the three solutions are summarized in Table 14.2.

TABLE 14.2. Comparative properties of the three solutions—true solution, colloidal solution and suspension

Property	*True solution*	*Colloidal solution*	*Suspension*
Diameter of particle	1·0 nm	range form 1—100 nm	100—500 nm
Appearance of particles	Invisible even through microscope	Invisible through microscope. Their scattering effect has been characterized through ultramicroscope	Visible
Separation of particles	Cannot be separated by any means	Can only be separated by ultracentrifugation	Can be separated by ordinary filtration
Diffusion of particles	Diffuse rapidly through a parchment membrane	Diffuse slowly through a parchment membrane	Cannot diffuse
Tyndall effect	No	Yes	Yes
Brownian movement	No	Yes	Yes

Colloidal particles are stable and do not settle out over a period as they are always in a rapid motion which offsets the gravitational effect. Because of their large surface area they exhibit adsorption phenomenon. The unbalanced forces on the surface of particles render them capable of adsorbing electrical charges in the form of either ions or electrons. This is generally accompanied by the secondary adsorption of more ions of the opposite charge (electrical double layer).

Since like charges are repelled, chances of aggregating into clusters are decreased, and thus, stability of colloidal particles remains ensured. At times, they form certain protective layers around them which also lessen their chances of aggregating into larger particles and precipitating. They possess certain optical and colligative properties.

In a colloidal solution, each particle is contained within its own boundary which separates it from the continuous dispersion medium. In a true solution, the solute and the solvent form one phase in which their respective molecules are randomly mixed.

The total surface area per gram of solid in a colloidal solution is very large. If one centimetre cube of a solid is broken into particles of 1 nanometre cube, the surface area becomes 6000 square metres. The surface to volume ratio increases 10 million times by the process of this subdivision. Adsorption on such a large surface imparts a number of unique properties to colloids.

Let us calculate this problem. One centimetre cube of a solid has a surface area 6×10^{-4} m². When it is broken into cubes of side one nanometre (10^{-9} m), area of each cube is 6×10^{-18} m².

$$\text{No. of particles} = \left(\frac{10^{-2}}{10^{-9}}\right)^3 = 10^{21}$$

$$\text{Total surface area} = (6 \times 10^{-18} \text{ m}^2) \times 10^{21}$$
$$= 6 \times 10^3 \text{ m}^2$$

Ratio of the final to initial surface areas $= 10^7$.

Because of the large surface area, adsorption by colloidal particles assumes great importance.

14.6. CLASSIFICATIONS OF COLLOIDAL DISPERSIONS

Colloidal state is not limited to dispersions of solid particles in a liquid medium, a gas or solid may also consitute the dispersion medium and the dispersed phase may be a gas, a liquid or a solid. but both cannot be gases. In the latter case they will dissolve homogeneously and a colloidal solution cannot be formed.

The possible colloidal systems or solutions (usually called sols) are summarized in Table 14.3.

Colloidal solutions are generally formed as sols. Sometimes colloidal states are differentiated on the basis of the dispersion medium employed, *e.g.*, dispersed phase in water is called **hydrosols.** Similarly,

Dispersed phase in alcohol—Alcosols

Dispersed phase in benzene—Benzosols

Dispersed phase in air —Aerosols

Colloidal systems may also be classified on the basis of interaction of phases (solvent affinity).

Sols are frequently divided into two classes : (*i*) **Lyophobic** (solvent hating), and (*ii*) **Lyophilic** (solvent loving). The lyophobic sols are those in which, if the dispersed phase is once coagulated cannot be re-dispersed by shaking them with the dispersion medium. Thus there is no appatent affinity between the dispersed phase and the dispersion medium. Sols of metals (*e.g.*, gold, sol, silver sol) metal hydroxides and metal sulphides (*e.g.*, arsenic sulphide sol)

TABLE 14.3. Some common colloidal systems

Dispersed phase	*Dispersion medium*	*Colloidal system*	*Example*
1. Solid	Gas	Solid aerosol	Smoke, dust storm, fumes
2. Solid	Liquid	Sols	Starch or proteins dispersed in water, some paints and inks, milk of magnesia, gold solution, muddy water ; As_2S_3, S, Fe_2O_3 and AgCl in water, white of an egg $Fe(OH)_3$ sol
3. Solid	Solid	Solid sol	Some alloys and minerals, ruby glass, black diamonds, certain natural and synthetic gems.
4. Liquid	Gas	Liquid aerosol	Mist, fog, cloud, insecticide spray
5. Liquid	Liquid	Emulsion	Milk, emulsified oils, creams, medicins, mayonnaise
6. Liquid	Solid	Solid emulsion	Cheese, jellies, gels, curd, butter boot polish, pearls $CaCO_3$ with H_2O inclusions), opal (SiO_2 with H_2O inclusions)
7. Gas	Liquid	Foam or froth	Foam, whipped cream, beaten egg whites, lemonade froth, soaps and detergents suds
8. Gas	Solid	Solid foam	Pumic stone (air in silicates), floating soaps, rubber, grey hair, biscuits, cake bread dough, lava, volcanic ash, occuluded gases

are examples of lyophobic sols. They are irreversible. In case water is the dispersion medium these are known as **hydrophobic sols.**

Such sols are easily precipitated (or coagulated) on the addition of small amount of electrolytes, by heating or agitation. They are preserved by adding stabilizing agents.

The **lyophilic colloids** include those sols which could be prepared with a disperse phase having affinity for the dispersion medium, *e.g.*. starch, gelatin, glue, proteins and agar when heated with water take up large quantities of water and form colloidal systems by **peptization**. Such colloidal systems are also called **emulsoids**. In lyophilic sols, the dispersed phase is not easily preci-

pitated and the sols are much more stable because of strong attractive forces operating between the suspended particles and the dispersion medium. After precipitation, they can be easily reverted to the colloidal state on shaking with the dispersion medium. Lyophilic sols are also called reversible sols. If water is the dispersion medium, they are called **hydrophilic sols**.

Disperse phases which easily form colloidal solutions are, at times, called **intrinsic colloids** and those which do not easily form colloidal solutions are called **extrinsic colloids**.

Table 14.4. lists some distinguishing features of the two types of sols.

TABLE 14.4. Comparison between lyophilic and lyophobic sols

Property	*Lyophilic sols*	*Lyophobic sols*
1. Dispersed phases	Mostly organic materials—gums, resins, shellace, proteins, high polymers, *etc.*	Mostly inorganic materials—finely divided metals, metallic oxides, sulphides and hydroxides, *etc.*
2. Stability and coagulation	Very stable due to attractive forces operating between the two phases. Not easily coagulated by hydroscopic materials, *e g.* alcohol, acetone, *etc.* Also coagulated by electrolytes in high concentration.	Less stable. Easily coagulated by adding electrolytes in small amounts, heating or agitation
	Reversible, *i.e.*, after coagulation may be dispersed again by adding dispersing phase	Irreversible ; once coagulated cannot be dispersed again by adding dispersing phase
3. Viscosity	High ; higher than that of dispersion medium	Low ; almost equal to that of dispersion medium
4. Surface tension	Lower than that of dispersion medium	Almost equal to that of dispersion medium
5. Hydration and stability	Highly hydrated ; stabilized by forces of solvation	Poorly hydrated ; stabilized by charge on the surface
6. Influence of electric field	Neutral and charged ; thus may or may not migrate towards electrodes	Charged ; hence migrate towards electrodes depending upon the charge
7. Visibility	Invisible even through ultramicroscope	Visible through ultramicroscope
8. Preparation	Prepared by simple and direct means	Prepared by indirect means

14.7. MULTIMOLECULAR, MACROMOLECULAR AND ASSOCIATED (MICELLES) COLLOIDS

The classification of colloids is also possible on the nature of dispersed phase. On this basis, colloids have been classified primarily in three classes :

Colloids
- Macromolecular colloids
- Multimolcular colloids
- Associated colloids

Macromolecular colloids. In these colloidal systems the dispersed phase is constituted by large molecules which are called macromolecules. These substances are highly polymeric with very high molecular masses. Their molecules are big enough to be of colloidal dimensions, and hence, display colloidal properties. Proteins (albumen, gelatin), polysaccharides and their derivaties (starch, cellulose) and other highly polymeric naturally occurring compounds are macromolecules. Their molecular masses range from thousands to millions. Synthetic compounds, *e.g.*, polyethylene, nylon, polystyrene, rubber, *etc.* are also macromolecules. Some of these macromolecules, *e.g.*, starch, gelatin, proteins, enzymes, *etc.*, constitute the dispersed phase in lyophilic sols, and thus, have typical colloidal properties. Many of them are crystalline in nature. Their colloidal solutions are quite stable and resemble true solutions in many respects.

Multimolecular colloids. In these colloidal systems, the dispersed phase is constituted by large aggregates of atoms or molecules which are formed as a result of aggregating properties of the dispersing particles. Thus, the dispersed phase may contain aggregates of different sizes and simple atoms or molecules. Their diameters do not exceed 1 nm. Such aggregates are called multimolecular colloids. Gold sol, hydrated ferric oxide sol, silicic acid sol, colloidal sulphur sol, metal hydroxides and sulphide sols, *etc.*, represent this system of colloidal state. Material constituting these sols are insoluble in water but under specific conditions could be made to exist in colloidal solutions.

Gold sol appears to have particles of varying sizes. This is because of the varying degree of aggregation of gold atoms. Sulphur sol also contains many such particles which contain a thousand or so of S_8 molecules. The aggregation of molecules have been possible due to weak van der Waals forces. Such multimolecules constitute the dispersed phase in lyophobic sols.

Associated colloids. Materials whose molecules aggregate instantaneously in the dispersing phase are called associated colloids. Such substances when present in high concentration in the dispersing phase yield thermodynamically stable molecular ionic aggregates

of colloidal dimensions. Such aggregates furnished (when in equilibrium with simple ions or molecules) in the dispersing phase are called **micelles**. Surface active materials, *e.g.*, soaps and detergents belong to this class of colloids. These substances furnish ions into solutions ; either one or both ionic species furnished may have colloidal dimensions. These associated colloids have both lyophilic and lyophobic groups. These groups/ions due to strong cohesion associate together to form micelles. Hundred or more molecules constitute micelles.

Sodium palmitate, a soap, on dissolving in water dissociate into Na^+ and palmitate ions. Palmitate ions get together and emerge as ionic micelles having colloidal dimensions. These micelles impart colloidal character to soap.

Cleansing action of soap

A typical salt present in soap is sodium octadecanoate (sodium stearate),

$$CH_3(CH_2)_{16}COO^-Na^+$$

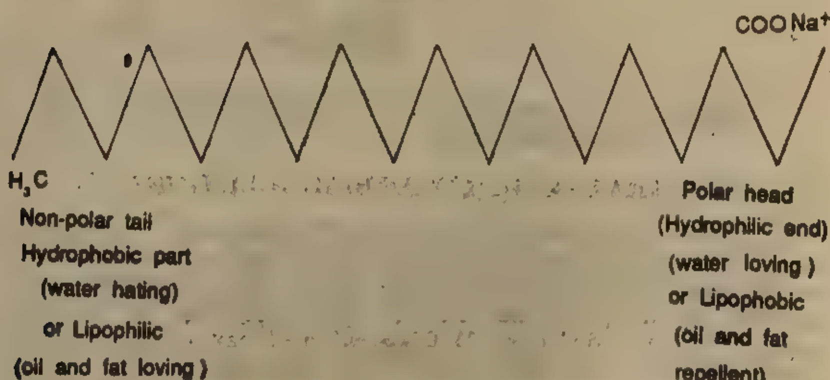


Fig. 14.8

Soap cleanses because it can emulsify fats and oils, *i.e.*, converts them into a suspension of tiny droplets in water. Oils present in skin react with dirt and form a greasy layer over the skin.

Fabrics also hold dirt by a thin film of oil or grease. Thus, the oil film must be removed before the dirt can be rinsed away.

Soap owes its emulsifying action to the combination of polar and non-polar group in its structure. When soap is added to water,

the hydrophilic carboxylate ions ($-COO^-$) dissolve in water and the hydrocarbon end dissolves in the oil (non-polar). Soap ions arrange themselves round each droplet of oil in the form of spherical clusters called micelles (Fig. 14.9). Such an orientation of cleansing agent at the interface between the dirt particles and the water decreases the interfacial or surface tension. The forces between water and oil (or grease) are thus much increased, so that the micelle can be lifted off the surface in the form of globules which can be washed away. As the surface of each micelle is negatively charged, the globules repel one another and do not coalesce. Thus soap acts as surface active substance.

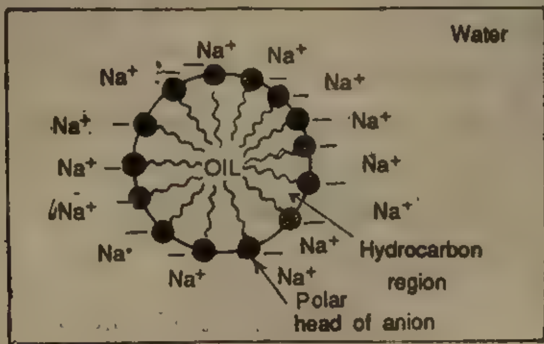


Fig. 14.9. A soap micelle in water medium—a drop of oil surrounded by soap ions

14.8. PREPARATION OF COLLOIDAL SOLUTIONS

Since colloidal particles have sizes between those of solutes in true solution and those of particles in coarse suspension, two general methods can be adopted for their preparation : (1) **Condensation**—building up of colloid-size particles from particles, of that are present in true solutions. (2) **Dispersion**—breaking up of large particles to colloidal size in a suspending medium.

(I) LYOPHOBIC SOLS

14.8.1. Condensatian Methods

These are based on the principle that the substances present initially in the atomic or molecular state are made to aggregate to colloidal state. This can be done by (*a*) chemical methods, and (*b*) physical methods.

(*a*) **Chemical Methods**. In these methods some chemical reactions are involved ; one of the products formed in reaction is normally insoluble in the dispersing medium. Insoluble product does

not coagulate but remains dispersed as colloid. Some of the reactions involved are given below :

(*i*) **Oxidation**. A colloidal solution of sulphur can be obtained by bubbling H_2S through an aqueous solution of sulphur dioxide or some other oxidizing agent such as bromine water, nitric acid, *etc.*

$$H_2S(g)+Br_2(l) \longrightarrow \underset{(Sol)}{S}+2HBr\ (aq)$$

$$SO_2+2H_2S \longrightarrow 2H_2O + \underset{(Sol)}{3S}$$

A sol of sulphur can also be obtained when oxygen is bubbled through a solution of H_2S. Colloidal sulphur can also be obtained by adding a concentrated solution of $Na_2S_2O_3$ to concentrated H_2SO_4. On cooling colloidal sulphur is obtained. This sulphur on dissolving in water constitutes a sulphur sol. **Selenium sol** can also be prepared by oxidizing H_2Se.

The colloidal solution thus obtained is purified by **dialysis.**

(*ii*) **Reduction**. Certain sols, *e g.*, **gold sol** can be formed by the reduction of very dilute solution of gold chloride with formaldehyde, glucose, hydrazine, stannous chloride or ferrous sulphate.

$$2AuCl_3 + 3SnCl_2 \longrightarrow 3SnCl_4 + \underset{(Sol)}{5Au}$$

Sols of silver and platinum are also produced by reduction technique. Sols so obtained are generally coloured (colour depends upon the size of particles).

(*iii*) **Hydrolysis.** Sols of hydrated oxides of weakly electropositive metals like iron, aluminium, tin, *etc.*, can be obtained by hydrolysis. A dark red colloidal suspension of ferric hydroxide sol may be obtained by pouring a freshly prepared saturated solution of ferric chloride in boiling hot water. To ensure the hydrolysis the mixture is heated for sometime. The sol is dialyzed in a parchment bag against warm water to free from HCl and undecomposed $FeCl_3$.

$$FeCl_3+3H_2O \longrightarrow \underset{(Sol)}{Fe(OH)_3}+3HCl$$

(*iv*) **Double decomposition**. Colloidal solutions of silver halide are produced by the reaction of dilute solutions of silver salts with alkali halides in equivalent amounts.

$$AgNO_3+NaCl \longrightarrow AgCl + NaNO_3$$

An orange coloured sol of As_2S_3 is produced by bubbling H_2S through a dilute solution As_2O_3 in water.

$$As_2O_3 + 3H_2S \longrightarrow \underset{(Sol)}{As_2S_3} + 3H_2O$$

A colloidal dispersion of silicic acid is obtained by treating a solution of sodium silicate with dilute HCl.

$$Na_2SiO_3 + 2HCl \longrightarrow \underset{(Sol)}{H_2SiO_3} + 2NaCl$$

Sometimes ions in very high concentration on mixing will produce particles of colloidal size, *e.g.*, colloidal $BaSO_4$ is produced by mixing Ba^{2+} and SO_4^{2-} ions in very high concentrations ($\sim > 4M$).

(*b*) **Physical Methods.** These do not involve any chemical reactions.

(*i*) **By exchange of solvent.** Phosphorus and sulphur are highly soluble in alcohol but insoluble in water. Their colloidal sols can be prepared by pouring their alcoholic solutions drop by drop in water. Alcohol is removed by dialysis. A milky colloidal solution of phenolphthalein indicator results when its alcoholic solution is poured into water. Such solutions are unstable.

(*ii*) **By change in physical state.** Sols of mercury and sulphur are produced by passing their vapours through cold water. Ammonium citrate is mixed to stabilize the solution.

(*iii*) **By controlled condensation.** Certain insoluble substances give colloidal solutions by their precipitation in the presence of some protective colloidal systems (*e.g.*, starch, gelatin, glycerol, glucose, *etc.*). Prussian blue sol is produced by precipitating it in the presence of starch.

14.8.2. Dispersion Methods

In these methods large particles are broken down to a colloidal size in the dispersing phase by some appropriate mechanical means. These unstable solutions are stabilized with a stabilizer. Dispersion may be achieved in the following ways :

(*i*) **Mechanical grinding (colloid mill).** Coarse particles of a substance are broken into smaller particles of colloidal dimensions in the dispersion medium by grinding them between two metal plates of a colloid mill (Fig. 14.10). The colloidal solution obtained is stabilized by adding a protective colloid. **Indian ink** (lamp black suspended in water) is prepared by this method. It is stabilized by adding gum arabic. **Paints** and **pigments** are also produced by this method.

(*ii*) **Electrical Dispersion or Bredig's Arc Method.** Colloidal metal sols of gold, silver, platinum, *etc.*, are prepared by this method. An electric arc (Fig. 14.11) is struck between the two closely set wires of metals (to be dispersed) under water containing

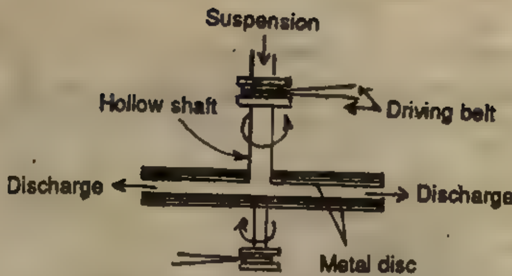


Fig. 14.10. A simple representation of colloid mill : the discs move at high speed in opposite directions

some protective colloidal material (NaOH or Na_2CO_3 prevents coalescing, *i.e.*, precipitation of metallic particles). The intense heat of arc disintegrate metallic wires into small pieces and form vapours. The vapours condense to particles of colloidal size. With active metals dispersion medium other than water is used.

Some atomizers produce sols by a spraying process. Powdered milk having colloidal size particles is prepared by dehydrating milk spray.

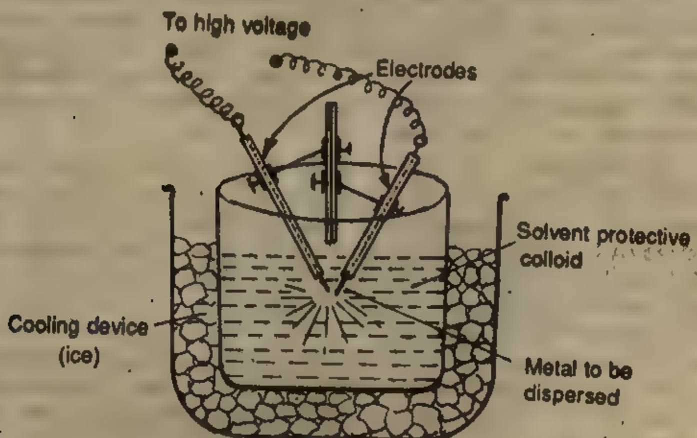


Fig. 14.11. Bredig's arc for preparing metallic dispersion in water.

(*iii*) **Peptization**. Peptization is the process by which certain substances (formed as a result of accumulation of colloidal size particle) are dispersed to the colloidal state when shaken with water containing very small amount of an electrolyte, which acts as the **peptizing agent**.

Freshly precipitated (suspension) AgCl in the presence of water containing some electrolyte ($AgNO_3$ having an ion common with AgCl serves as peptizing agent) becomes colloidal on shaking

strongly. The particles of suspension adsorb ions and become charged, and thus, break up.

$$\underset{\text{(Suspension)}}{AgCl} + \underset{\text{(Peptizing agent)}}{Ag^+} \longrightarrow \underset{\text{(Sol)}}{AgCl.\ Ag^+}$$

Ferric hydroxide and aluminium hydroxide sols can be prepared by using $FeCl_3$ and $AlNO_3$ (or HCl) respectively as peptizing agent.

$$\begin{matrix}\text{Freshly} \\ \text{precipitated}\end{matrix} \left[\begin{matrix} Fe(OH)_3(s) + Fe^{3+} \longrightarrow Fe(OH)_3 . Fe^{3+} \\ Al(OH)_3(s) + Al^{3+} \longrightarrow Al(OH)_3 . Al^{3+} \end{matrix}\right] \text{Sol}$$

II. LYOPHILIC SOLS

These are the solutions of intrinsic colloids, *e.g.*, gelatin, starch, dyestuffs, high polymers, gum arabic, egg albumen, soaps, glycogen, *etc.*, in dispersing phase. Such solid substances (already in colloidal size) when brought in contact with water, simply disperse instantaneously to form colloidal systems and are said to undergo peptization. Sometimes heating is also required.

These sols are reversible in nature and stable. **Collodion,** a sol of cellulose nitrate is prepared by using a mixture of ethanol and ether (dispersing phase).

14.8.3. Purification of Colloidal Solutions

Colloidal systems (particularly lyophobic sols) generally contain some added impurities, *e.g.*, impurities of electrolytes and other substances. These impurities make the sol unstable. It is necessary to reduce their concentrations in a judicious way otherwise they would coagulate the colloidal dispersions. Methods generally used for the purpose are as follows :

(*i*) **Dialysis.** It is the filtration device of separating colloidal dispersions from particles of impurities present in solution. It consists of a membrane (called semipermeable as it permits the passage of one type of particles) having extremely small pores in which sol is filled. It is kept immersed in pure water. It permits small ions of electrolytes present in solution to pass through but retains the colloidal particles. This is a slow process. The process can be speeded up by using warm water [Fig. 14.12 (*a*)]. The dialysis can be further accelerated by applying a potential difference across the membrane. Under the influence of electric field, ions migrate at a much faster rate than in a simple dialysis. The electrodialyzer used is shown in Fig. 14.12 (*b*). At times, the container is divided into three compartments. The middle compartment (made of semipermeable membrane) is filled with sol and the other two are filled with pure water. In practice, cellophane, collodion, animal bladders and parchment are used as dialyzing membranes.

(*ii*) **Ultrafiltration.** It is a process similar to filtration, except that a membrane is used which permits the passage of electrolyte and dispersion medium and not the colloid. Ordinary filter paper is

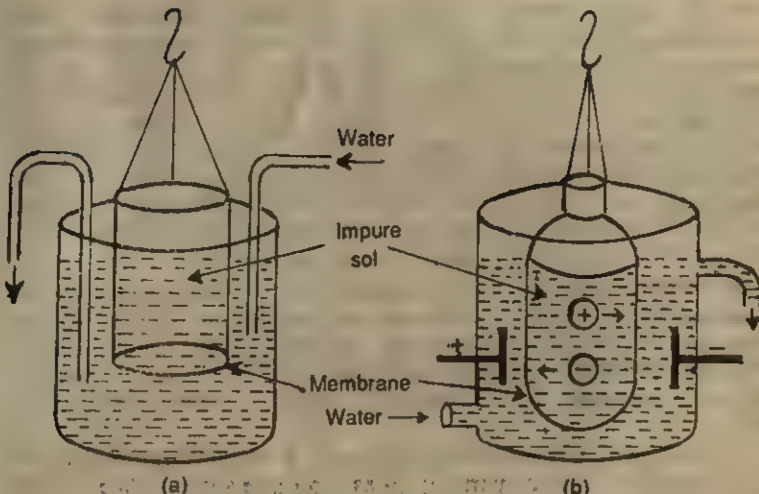


Fig. 14.12 (a) A dialysis cell (b) Electrodialysis

permeable to colloidal dispersions as well as to electrolytes, and thus, cannot be employed for filtering sols. However, a filter paper impregnated with colloidion or gelatin solution (called ultrafilter) serves the purpose. Due to this treatment the pore size of the filter paper is reduced. By using the impregnating solution of different concentrations a series of graded ultrafilters can be obtained. On filtering the sol through such ultrafilters, colloidal particles are retained in the form of slime. Slime on treating with water disperses spontaneously to form a colloidal system.

14.9. PROPERTIES OF COLLOIDAL SOLUTIONS

A reference to the usual properties like, size, filterability, detection, character, *etc.* have already been made in Section 14.5.

The distinct characteristic properties of colloidal particles can be classified as follows :

1. Particulate (particle-like) properties
2. Optical properties
3. Electrical properties

1. Particulate Properties

Colour. The colour of the sol is not always the same as that of the substance (constituting the dispersed phase) in bulk. The size and shape of the particles affect the colour. Spherical particles impart red colour to gold sol but elogated and flat particles blue colour. Sulphur sols may be colourless, light yellow or deep yellow in reflected light and reddish in transmitted light.

Colligative properties. These properties depend upon the number of moles present. Colloidal particles have a very high average molecular masses, and hence, the number of moles present in solution will be extremely low. Thus, the value for any of the colligative properties for a specific substance will be low compared to its value when it forms a part of true solutions. However, some colloids have a measurable osmotic pressure. The osmotic pressures of some lyophilic colloids, *e.g.*, proteins, cellulose, high polymers starch, gelatin, *etc.*, have been determined with a reasonable degree of accuracy. The data of osmotic pressure has been used to determine the average molecular mass of colloidal particles.

Brownian motion. Colloidal particles in a dispersion medium are constantly in motion in zig-zag paths (Fig. 14.13) because of similar motion of solvent molecules colliding with them. This is known as **Brownian motion**, after Robert Brown who observed (under a microscope) this behaviour in pollen grains suspended in water.

At any given instant a colloidal particle may be bombarded by more molecules from dispersing phase on one side and less on the other. Now the colloidal particle may shift its path at one time in one direction at another time in some other direction and so on, because of the difference in kinetic energy imparted by dispersing phase molecules to the colloidal particles. Hence, the visible motion results. The erratic motion tends to preserve a uniform distribution of the particles throughout the system.

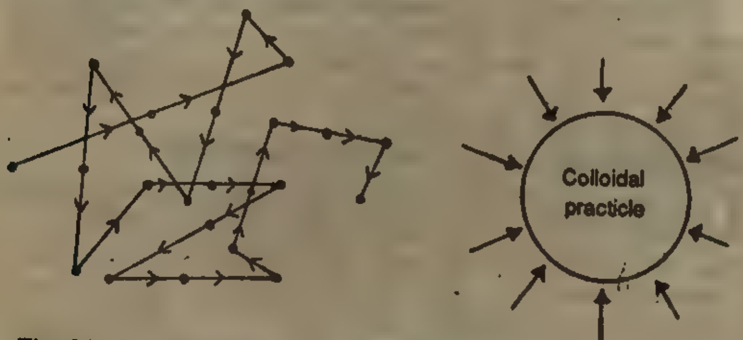


Fig. 14.13. Colloidal particle exhibiting the Brownian movement

Diffusion. Colloidal particles, like solute particles, diffuse from a region of higher concentration to that of lower concentration until equilibrium is achieved. Because of their mass, they move slowly, and thus, the rate of diffusion will be low. The process can be used to separate colloids from colloids of different sizes and also to find out their sizes and hence their particle masses.

Sedimentaion. Under the influence of gravity, the sol particles tend to settle down very slowly. This rate of settling down

or sedimentation can be accelerated by the use of a high speed centrifuge called **ultracentrifuge.**

2. Optical Properties

Light passes through a true solution without producing a visible path. But a beam of light directed through a colloidal dispersion is often visible because of the light scattered by the colloidal particles. This phenomenon is known as the **Tyndall effect** after the English physicist who first discovered it. When a beam of light is passed through a sol, the liquid will appear as in Fig. 14.14 when viewed at right angles to the beam of light.

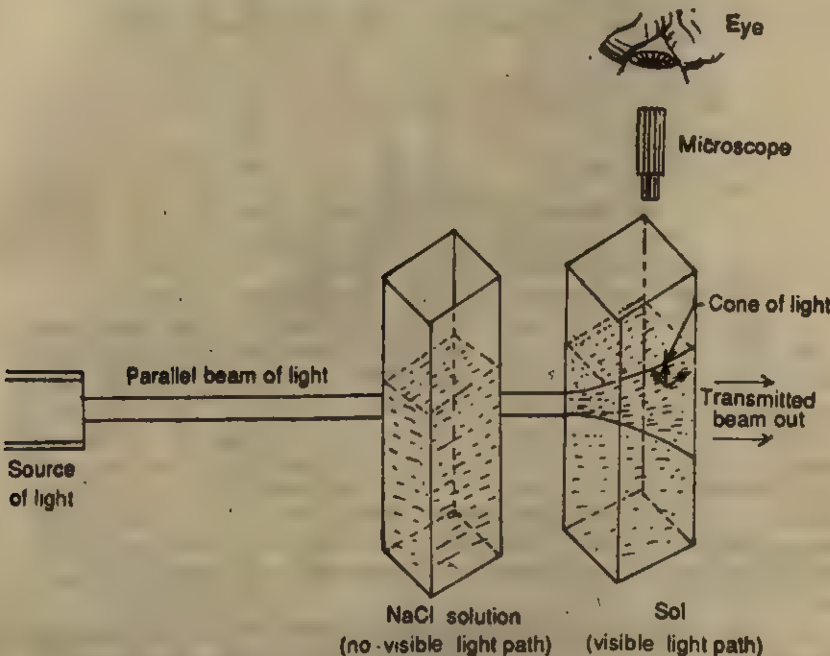


Fig. 14.14. The Tyndall effect : Light scattering occurs in the colloidal sol but not in NaCl solution

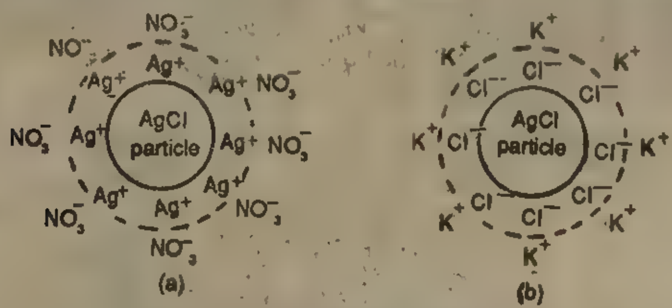
This is why, the fog, a dispersion of water droplets in air scatters the light. The pattern of colours in a sunset, the colour of the sky and the colour of the human eye are the consequences of selective scattering of light. A beam of light from a spotlight is visible on a foggy night but not on a clear one.

3. Electrical Properties

Colloidal particles acquire a surface electric charge when in contact with a polar dispersion medium such as water, or an electrolyte, such as an aqueous salt solution. The adsorption of ions on to colloid particles is dependent open many factors including the

presence of ions common to the colloid particles and the dispersion medium.

For example, solid AgCl in a solution of $AgNO_3$ attracts Ag^+ ions, giving positively charged particles [Fig. 14.15(*a*)], while in a solution of KCl attracts Cl^- ions giving negatively charged particles [Fig. 14.14(*b*)].



Building up of Helmholtz double layer
Fig. 14.15. Adsorption of ions from sol.
(*a*) *AgCl precipitated in the presence of excess of Cl^-*
(*b*) *AgCl precipitated in the presence of excess of Ag^+*

Thus the nature of ions to be adsorbed depends upon the method of preparation, *e.g.*, if KCl is added to $AgNO_3$, KCl will remain in solution. Thus, AgCl will adsorb Cl^- ions. All particles in a colloidal system carry the same kind of charge. Thus, particles present in a colloidal system will be either positively or negatively charged. The similar charges on the particles keep them dispersed as like charges repel each other. Thus, the system tends to remain stable. At times particles capture electrons from air and during electrodispersion method (Bredigs' arc method). The charge on colloidal particles also arises from the ionization of groups present on the surface.

Thus, there are various mechanisms by which colloid particles acquire a charge, the sign of which can be detected by cataphoresis or electrophoresis (Fig. 14.16). When a sol is placed in an electrolytic cell, the dispersed particles move towards the cathode or anode under an applied electric field depending on whether they are positively or negatively charged (Table 14.5). The migration of charged

TABLE 14.5. Solutions with their electrical charge

Positively charged	*Negatively charged*
Hydroxides—Fe $(OH)_3$, $Al(OH)_3$, Cr $(OH)_3$	Metallic sols of Au, Pt, Cu, Ag, *etc.*
Oxides—TiO_2	Sulphur, the sulphides, *e.g.*, As_2S_3, CdS, *etc.*, silicic acid.
Proteins in acid solution	Organic colloids, *e.g.*, starch, gelatin *etc.*
Basic dyes—methylene blue, *etc.*	Acid dyes—eosin, *etc.*

colloidal particles under the influence of electric field is called electrophoresis. During electrophoresis, the colloidal particles more towards one electrode and the dispersion medium moves towards the other.

Sols of metallic oxides and hydroxides are usually positively charged and migrate towards the cathode electrode, while sols of metals, sulphur, metallic sulphides are usually negatively charged and migrate to the anode under electrical potential gradient.

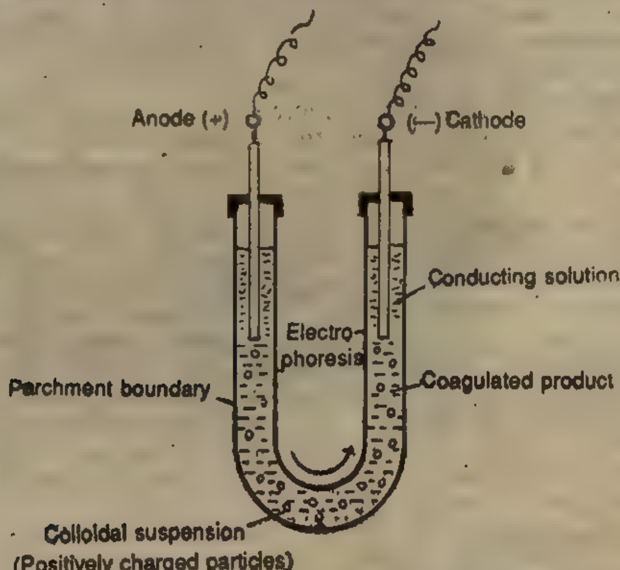


Fig. 14.16. Representation of electrophoresis

The migration of charged colloidal particles in an applied field forms the basis of electrodeposition of colloids. Rubber gloves and other intricate rubber articles are produced by electroplating moulds with colloidal dispersions of rubber. Colloidal particles dispersed in drinking water are also removed by this method.

The smoke and dust particles present in discharge of chimneys are often colloidally dispersed and carry some charge. These particles can be precipitated out by passing the chimney's discharge through high voltage plates. They get discharged on electrodes and coagulate. This principle has been adopted in Cottrell's smoke/dust precipitator.

14.9.1. The stability and Coagulation of Lyphobic Sols

The stability of colloidal solution is due to the repulsive forces set up between the charged particles. The stability of a sol is increased by the presence of a small amount of electrolyte.

In presence of large concentrations of electrolytes, colloidal particles lose their charge and aggregate to form a precipitate. The

point at which the coagulation takes place is called the **isoelectric point**.

(*i*) Coagulation of colloidal particles is caused effectively by the ions carrying opposite charge to that of colloidal particles.

(*ii*) Coagulation power of electrolytes (ions) increase appreciably with increase in size of the charge on ions causing coagulation. These general observations together are known as **Hardy Schulze rule**. The highly charged ions such as Al^{3+} are the most effective in coagulation. Hence aluminium salts are used in preparations to stop bleeding from small cuts by coagulation, as blood is a negative colloid.

Lyophilic colloids are much more resistant to coagulation, and a lyophillic colloid may be added to a lyophobic colloid (of the same charge) to stabilize the latter. This is termed **protective action.**

Colloidal dispersion of silver halides in photographic films is preserved by using gelatin as protective colloid. Gum arabic is employed in the stabilization of certain inks. A gold solution can be stabilized by gelatin, gum or starch colloid. The protective power of colloid is expressed in terms of gold number (introduced by Zsigmondy). It is defined as the minimum number of milligrams of the dry protective colloid which will check the coagulation of 10 mL of a standard red gold sol (*i.e.*, prevent its colour becoming blue) on adding 1 mL of a 10% sodium chloride solution. Obviously, the smaller the gold number of a lyophilic colloid, the greater is its protective power.

14.10 EMULSIONS

A liquid dispersed in a liquid dispersing medium is known as emulsion. Milk, the most common example of an emulsion, is simply fine particles of fat suspended in an aqueous medium. It also contains casein which stabilizes the emulsion. Here casein works as emulsifier and is called **emulsifying agent**. This emulsion belongs to oil-in-water type emulsicns. Water in-oil is another type of emulsion Butter is an example of this class, where fine particles of water are disseminated in a medium of fat.

The droplets present in emulsions can be somewhat larger than the suspended particles in sols.

An emulsion may be prepared by shaking together two immiscible liquids vigorously. The process of agitating breaks one liquid into droplets of colloidal dimensions which, in turn, are dispersed through the body of the other liquid. The droplets of dispersed liquid tend to flocculate forming clusters of droplets which are too large to remain in the dispersed condition. As a result, the two liquids soon separate into two layers. Sometimes, a mixture of two liquids is subjected to ultrasonic vibrations. Emulsions are generally unstable. They may be stabilized by adding some emul-

sifying agent. These emulsifying agents decrease the surface tension of the two liquids, and thus, the tendency of the tiny drop lets to coalesce and form aggregates is reduced. They may also form protective layers around colloidal liquids.

Soaps and detergents are the commonly employed emulsifying agents. Among other stabilizing agents include proteins, gum, agar, *etc*. The emulsifying properties of soaps and detergents have impact in washing of clothes and crockery. The owe their cleansing ability to the structures of their molecules which allow them to assume the role of emulsifying agents between dirt, grease or oil and water. The dispersed particles of soap adsorb (emulsify) fine particles of dirt and form a protective film about them. Thus, the dirt particles are held in suspension and are washed away (Section 14.7).

Emulsification helps in the digestion of fats in the intestines. Intestines also contain some alkaline solution A small amount of fat reacts with alkaline solution forming a sodium soap which emulsifies the remaining fat, and thus, digestive enzymes are helped by emulsification in carrying out their metabolic functions.

Mayonnaise, an emulsion of olive oil in vinegar, is stabilized by egg yolk. Among cosmetics and pharmaceuticals, various lotions, face creams, ointments and other such preparations are emulsions of oil-in-water or water-in-oil type. Many oily drugs are available in the form of emulsions.

Emulsions find various applications in industries. The froth flotation process for the concentration of ore is the practical application of adsorption. In this the finely divided ore lying in a water tank is treated with oil. On agitating, oil disperses into colloidal particles which have a stronger adsorptive attraction for the metallic particles than for the gangue particles. Oil particles stick to ore particles and move up in the form of the foam leaving behind gangue.

Emulsions sometimes do not serve useful purposes, *e.g.*, petroleum obtained from oil is always emulsified with water. Emulsions are broken to recover the constituent liquids by physical methods like freezing, boiling, filtration, electrostatic precipitation or by centrifugation. Chemical methods can destroy the stabilizing (emulsifying) agents. Centrifugation method is employed to separate cream from milk.

14.11. CATALYSIS

The word **catalysis** (Greek katalysis, "dissolution, release") was coined by Berzelius in 1835. Wilhelm Ostwald defined a catalyst as follows :

'A catalyst is a substance that increases the rate of a chemical reaction without itself being permanently changed'.

There is another term **inhibitor** which is used for those substances that slow down the rate of reactions. Since the catalyst remains chemically unchanged at the end of the reaction and does not affect the equilibrium constant, its effect is restricted to the factor controlling the rate of a reaction, *i.e.*, the activation energy. Thus, the catalyst speeds up a reaction by reducing the activation energy (Ea) of the reaction. Since the equilibrium constant remains constant, the catalyst must affect both the forward and backward reactions equally, and the onthalpy charge (ΔH) must remain unchanged (Fig. 14.17).

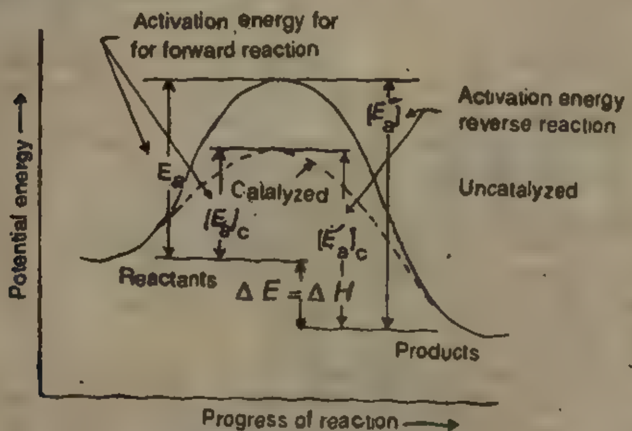


Fig. 14.17. The role of a catalyst in reducing the activation energy

Thus, the effect of a catalyst in increasing the rate of a reaction is to provide an alternate path way with a lower energy requirement (lower activation energy). Because of the lower energy barrier (Fig. 14·18), a greater fraction of the reactant molecules will possess the minimum kinetic energy required for reaction than in the uncatalyzed reaction. This will make the reaction to proceed at a faster rate. The manner in which a catalyst modifies the pathway for a reaction depends on the nature of the particular reactants and the catalyst.

There are two main types of catalytic reactions: homogeneous and heterogeneous.

Homogeneous Catalytic Reactions (Homogeneous Catalysis)

When the catalyst happens to be in the same phase in which reactant molecules exist, the reaction is known as a homogeneous catalytic reaction, and the process is called homogeneous catalysis.

In homogeneous catalytic reactions the catalyst is homogeneously mixed with the reactant molecules. Following examples may be given.

(*i*) Oxidation of sulphur dioxide in presence of nitrogen oxides (catalyst) in the manufacture of sulphuric acid :

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO + 2SO_2 \longrightarrow 2SO_3 + 2NO$$

(*ii*) Oxidation of I^- in the aqueous solution by $S_2O_8^{2-}$ ions in the presence of Fe (II) ions.

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$$

Oxidation of Fe^{2+} to Fe^{3+}

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

Reduction of Fe^{3+} to Fe^{2+}

(*iii*) Acid hydrolysis of cane sugar. Here H^+ ions act as a catalyst.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

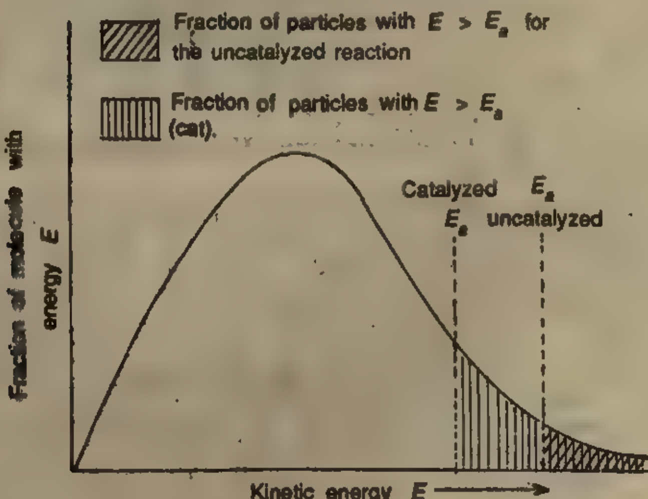
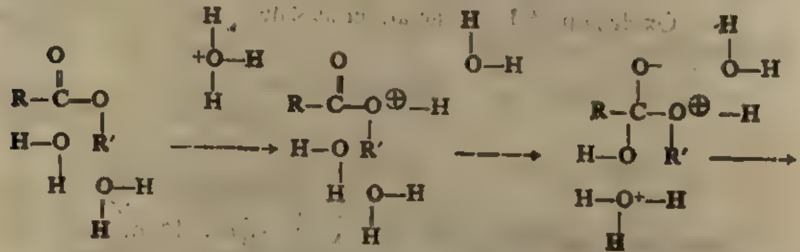


Fig. 14.18. Energy distribution in a collection of molecules. The lower activation energy of a catalyzed reaction makes possible for a larger fraction of the molecule to cross the energy barrier.

(*iv*) Hydrolysis of an ester in presence of hydrogen ions :

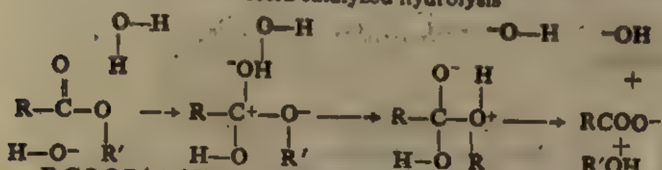
$$CH_3COOC_2H_5+H_2O \xrightarrow{H^+} CH_3COOH+C_2H_5OH$$

Perhaps the commonest form of homogeneous catalysis is **acid-base catalysis.** Many reactions in solution phase are catalyzed by acids, *i.e.* H^+ ions, as well as by bases, *i.e.* OH^- ions. The best examples to illustrate this are the hydrolysis of an ester. The mechanisms of acid and base catalyzed reactions are illustrated below :



$$RCOOR'+H_2O+H_3O^+ \longrightarrow RCOOH+R'OH+H_2O+H_3O^+$$

Acid catalyzed hydrolysis



$$RCOOR'+2H_2O+OH^- \longrightarrow RCOOH+R'OH+OH^-$$

Base catalyzed hydrolysis

Heterogeneous Catalytic Reactions (Heterogeneous Catalysis or Contact Catalysis)

When the reactants and the catalysts happen to be present in different phases, it is known as heterogeneous catalytic reaction or **heterogeneous catalysis or contact catalysis**. In hetergeneous catalytic reactions, the reaction occurs at the surface of the catalyst, and hence the name **contact catalysis**. The larger the surface of the catalyst, the greater is its activity. The surface area of the catalyst can be greatly increased by breaking the catalyst into smaller particles. Thus, it is found that finely divided platinum is a more effective catalyst than a platinum foil. Following examples of heterogeneous catalysis can be given :

(*i*) Dehydration of alcohol in presence of finely divided nickel

$$C_2H_5OH \xrightarrow{Ni} H_2O+CH_2=CH_2$$

(*ii*) Oxidation of sulphur dioxide to sulphur trioxide in presence of vanadium pentoxide in the manufacture of sulphuric acid by contact process.

$$2SO_2+O_2 \xrightarrow{V_2O_5} 2SO_3$$

(*iii*) Hydrogenation of vegetable oil in presence of finely divided nickel to obtain vanaspati ghee.

(*iv*) Synthesis of ammonia by Haber process in presence of ferric oxide catalyst

$$2N_2+3H_2 \xrightarrow{Fe_2O_3} 2NH_3$$

(*v*) Oxidation of carbon monoxide in automobile exhaust by platinum catalysts.

(*vi*) Cracking of hydrocarbons in the presence of hydrogen by zeolite catalysts.

(*vii*) Polymerization of ethylene on $TiCl_4$ and trialkylaluminium (Ziegler method).

(*viii*) Reaction of producing hydrocarbons by CO and H_2 on iron or cobalt catalysts (Fishcher-Tropsch Process).

(*ix*) Synthesis of CH_3OH from CO and H_2 using $(ZnO+CuO)$ as catalyst.

In all the examples cited above, the catalyst is usually in the solid phase, and all the reactants in the gaseous or liquid phase. A reaction between gaseous subtances at a solid catalyst interface is prefaced by adsorption of the gases on the solid in such a way that reaction is encouraged. The reactant molecules may get adsorbed as such or they may get fragmented on the catalyst surface. For example, carbon monoxide gets adsorbed as a molecule, on the surface of finely divided nickel. However, it generally breaks up into carbon and oxygen atoms on the surface of iron or manganese catalyst. Such a dissociation is at times necessary for many reactions to take place.

Adsorption occurs at the active sites on the surface of the solid. Active sites are created by excess attractive forces along crystal edges and grain boundaries. Finely divided solid contains enough active sites.

Reaction generally occurs in the following stages :

(*i*) Diffusion of the reactants to the catalyst,

(*ii*) Adsorption on the catalyst surface,

(*iii*) Making and breaking of bonds,

(*iv*) Desorption of products from the catalyst, and

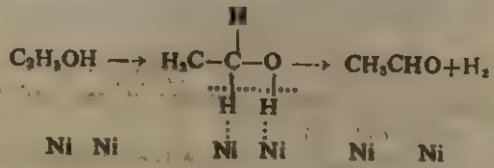
(*v*) Diffusion of products away from the catalyst.

14.11.1. Nature of Solid Catalyst

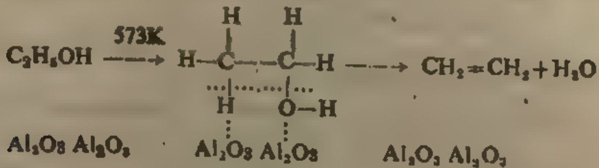
Various types of solids are used as catalyst : metals, alloys, metal oxides, metal sulphides, clays, *etc.* Catalysts may be pure substances or mixtures of substances. They may be crystalline, microcrystalline (fine particles) or amorphous.

Since the positions of active sites are determined by the crystal structure of the catalyst and depend upon its chemical nature, catalysts are specific for given reactions. For example nickel is widely used for dehydrogenation, and alumina for dehydration, even of the same material.

Surface of catalyst

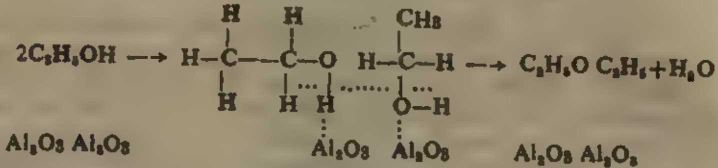


Surface of catalyst



Below 573 K, ether is formed.

Surface of catalyst



Thus catalysts are selective in directing a reaction to yield particular products. This is termed their selectivity. For example, n-heptane selectively gives toluene (n-$C_7H_{16} \longrightarrow C_6H_5CH_3$) on a platinum catalyst. Similarly, $CH_3CH{=}CH_2$ (propylene) $+O_2$ give $CH_2{=}CHCHO$ (acrolein) selectively over bismuth molybdate catalyst.

14.11.2. Shape-selective Catalysis

The cracking of hydrocarbons is generally catalyzed by using silica or alumina. Metal oxides catalysts are widely used in dehydrogenation of saturated hydrocarbons to form unsaturated hydrocarbons, for example butadiene. The most important oxide catalysts today are **zeolites**. They are used as catalysts in the petroleum industry for cracking of hydrocarbons and isomerization. The zeolites (Unit 2) are a class of aluminosilicate possessing a porous, open network. Because of this structure, zeolites provide a large surface area.

Reactions in zeolites depend on the size of the cavities (cages) and pores (apertures) present in them. The significant feature of zeolite catalysis is the **shape-selectivity**, which depends on the pore structure. The pore size in zeolites generally varies between 260 pm and 740 pm. Depending on the size of the reactant and

product molecules compared to size of the cages or pores of the zeolite, reactions proceed in a specific manner.

Pores are created when zeolites are heated. These pores can trap small molecules such as H_2O, CO_2, CH_3OH or NH_3. Such molecules are reversibly adsorbed by the dehydrated zeolites, known as **molecular sieves**.

There is a zeolite catalyst (called ZSM-5) which is used to convert alcohols to gasoline (petrol). It dehydrates the alcohol. Shape-selectivity in this reaction can be judged from the data given in the Table 14.6 on the conversion of two alcohols to hydrocarbon mixtures.

TABLE 14.6

Product	*Starting with methyl alcohol* (CH_3OH) (*per cent*)	*n-heptyl alcohol* (n—$C_7H_{15}OH$) (*per cent*)
Benzene 1	1.7	3.4
Ethane 4	0.6	0.3
i-butane 2	18.7	19.3
i-pentane 6	7.8	8.7
Methane 5	1.0	0.0
n-butane 3	5.6	11.0
Toluene 7	10.5	14.3
Xylenes 8	17.2	11.6

The product distribution depends on the size of the pores to accommodate linear and iso-alkanes as well as benzene derivatives.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

14.1. Choose the correct answer of the four alternatives given for the following questions :

(*i*) Which of the following properties does not belong to a chemical adsorption ?

(*a*) highly specific

(*b*) reversible

(*c*) dependent on the surface area of adsorbent

(*d*) depends upon temperature.

(*ii*) Which of the following expressions is applicable at intermediate pressures ?

(*a*) $\frac{x}{m} = kp^{n}$

(*b*) $\frac{x}{m} = kp^{1/n}$

(*c*) $\frac{x}{m} = k\,p^{0}$

(d) $\frac{x}{m} = kp^{n2}$

(iii) Which of the following properties is common to true solutions and colloidal dispersions ?
(a) Tyndal effect
(b) Brownian motion
(c) particles diffuse through a parchment membrane
(d) separation of particles is difficult.

(iv) Which of the following colloidal systems describe a liquid dispersed in gas ?
(a) mist (b) foam
(c) smoke (d) fume.

(v) Which of the following sols represent lyphilic colloid ?
(a) gold sol (b) silicic acid sol
(c) sulphur sol (d) gelatin sol.

(vi) Which of the following properties pertains to lyphobic sols ?
(a) stable
(b) coagulation process is irreversible
(c) both neutal and charged
(d) easy to prepare.

(vii) Which of the following materials is classified as associated colloid
(a) polysaccharide (b) ferric oxide
(c) rubber sol (d) soap.

(viii) Which of the following soles carry negative charge ?
(a) As_2S_3 sol (b) $Fe(OH)_3$ sol
(c) TiO_2 sol (d) $Al(OH)_3$ sol.

(ix) Milk is an example of
(a) suspension (b) foam
(c) emulsion (d) sol.

(x) A colloid can be purified by
(a) peptization (b) coagulation
(c) condensation (d) dialysis.

14.2. Fill in the blanks with appropriate words :

(i) Emulsions are colloidal systems containing............

(ii) Colour of the colloidal solution depends on..... ......

(iii) The amount of a gas adsorbed by a definite quantity of solid adsorbent is............

(iv) Catalysts act to increase the rates of reactions by providing an alternate pathway with a............

(v) Lattice defects at the surface of a solid help the process of............

(vi) Anhydrous silica gel possesses a large.........and has a good capacity for...........water and other substances.

(vii) Adsorption is an...........process and occurs with a decrease......... in...........

(viii) Colloidal particles are good...........as they provide a large surface area.

(ix) Lyophilic sols are also called...........sols.

(x) Colloidal particles diffuse from a region of...........concentration to that of......concentration.

14.3. **Which of the following statements are true (T) and false (F).**

(*i*) It is usually found that the concentration of molecules at the interface is greater than the concentration in the bulk of the phase.

(*ii*) A heterogeneous catalyst functions by bringing the reacting molecules into close cantact at the surface of the catalyst.

(*iii*) The adsorption isobars for physical and chemical adsorption are similar in nature.

(*iv*) Soaps and detergents are called surface active agents.

(*v*) Colloidal dispersions are always neutral in nature.

(*vi*) Light passing through a true solution is always visible as it is scattered by the particles present in solution.

(*vii*) Colloidal particles coagulate easily.

(*viii*) The migration of charged colloidal parricles under the influence of electric field is called electrodialysis.

(*ix*) A liquid dispersed in a liquid dispersing medium is known as emulsion.

(*x*) A semipermeable membrane permits the passage of one type of particles.

14.4. **Match the statements/terms given under column B against the terms given under Column A.**

Column A	*Column B*
(*i*) Milk	1. Carries positive charge
(*ii*) Ferric hydroxide	2. An emulsion
(*iii*) Hydrophilic solutions	3. A mechanicai method of preparing colloid.
(*iv*) Chemisorption	4. A process for dispersing of precipitate
(*v*) Physisorption	5. A gas in a liquid
(*vi*) Foam	6. A liquid in a solid
(*vii*) Gel	7. Commonly irreversible
(*viii*) Colloid mill	8. Emulsoids
(*ix*) Peptization	9. Forms molecular multilayers

SHORT ANSWER QUESTIONS

14.5. What happens when :

(*i*) A beam of light is passed through As_2S_3 sol

(*ii*) KCl is added to $Fe(OH)_3$ solution.

(*iii*) Electricity is passed through a colloidal solution.

(*iv*) Gelatin is added to gold sol.

(*v*) Colloidal solutions of Fe_2O_3 and As_2S_3 are mixed.

14.6. Explain the difference between sols and emulsions.

14.7. State a few reasons for the origin of electric charge on colloidal particles.

14.8. Why do adsorbed charges on colloidal particles act to prevent congulation and precipitation of a colloid ?

14.9. Frequently a preparation of a colloid, such as a protein can be mdae more stable if the colloid is dialyzed. Why is this so ?

14.10. How does the catalyst work ?

TERMINAL QUESTIONS

14.1. Explain the following :

(*i*) Surfaces of both liquids and solids are under the influence of unbalanced forces.

(*ii*) Colloidal particles show electrical properties.

(*iii*) The process of adsorption is faster than the absorption process.

(*iv*) The extent of adsorption depends upon the surface area of adsorbent.

(*v*) Coagulation of colloidal particles is caused by adding electrolytes.

(*vi*) Colloidal particles show Brownian movement.

14.2. Give two examples of each : (*a*) Lyophilic sols, (*b*) Lyophobic sols, (*c*) Emulsions, and (*d*) Emulsifying agents.

14.3. (*a*) Point out each of the following colloidal systems as hydrophilic or hydrophobic : gold sol, starch suspension, As_2S_3 sol, copper sol, egg albumen sol, sand suspended in water, sulphur sol and AgCl sol.

(*b*) Point out the dispersed phase and the dispersion medium in each of the following colloidal systems : smoke, fog, whipped cream, paint, pumic stone, milk, gem stones, sprays and starch suspension.

14.4. (*a*) Coagulation of colloidal solution is affected by the amount of an electrolyte and the size of the charge on ions. Comment.

(*b*) The extent of coagulation of As_2S_3 sol with $AlCl_3$, $BaCl_2$ and NaCl varies in the order $AlCl_3$, $BaCl_2$, NaCl. Explain.

14.5. (*a*) Colloidal systems cannot be separated from electrolytes by filtration Explain.

(*b*) Exte- led dialysis cause coagulation. Explain.

(*c*) Colloidal dispersions are good adsorbing agents. Explain.

14.6. Explain the phenomenon of adsorption. How does it differ from absorption.

14.7. Differentiate between in each of the following sets :

(*a*) Adsorbent and adsorbate.

(*b*) Chemisorption and physisorption.

(*c*) Dispersed phase ahd dispersion medium.

(*d*) Lyophilic and lyophobic solutions.

14.8. (*a*) Suggest the probable mechanism of adsorption.

(*b*) List the various factors which govern the degree of adsorption of gases on solids.

14.9. Explain the two terms—adsorption isotherms and adsorption isobars. Describe Freundlich's adsorption equation.

14.10. How does the extent of adsorption vary with temperature and pressure ? Explain.

14.11. Write short notes on : (*a*) Competing adsorption, (*b*) Catalytic reaction and adsorption, and (*c*) Adsorption from solutions.

14.12. Explain why adsorption is usually accompanied by decrease in enthalpy ? Why does adsorption stop after some time ?

14.13. What do you mean by colloidal solution and colloidal state ? How do colloidal solutions differ from true solutions with respect to dispersed particles, size, homogeneity, Brownian movement and Tyndall effect ?

14.14. What is the difference between dispersion and condensation methods for prepairing colloidal systems ? Describe two methods of each type.

14.15. How are colloids classified on the basis of (*a*) physical states of components, (*b*) nature of dispersion medium, and (*c*) association between dispersed phase and dispersion medium ?

14.16. Differentiate between multimolecular and marcromolecular colloids ? Give three examples of each of them. Describe associated colloids ? How do they differ from the other two types of colloids ?

14.17. (*a*) Describe two methods of purifying colloids.

(*b*) Suggest a method of preparing colloidal solution in water for each of the following : (*i*) Sulphur, (*ii*) $Fe(OH)_3$, (*iii*) Copper, (*iv*) Silver, and (*v*) $BaSO_4$.

14.18. Distinguish between true molecular solutions, colloidal dispersions and suspensions.

14.19. Give the various reasons for the electric charge on colloidal particles. What are the various consequences of electrical charge ?

14.20. (*a*) In what ways do the electrical charges affect the stability of a colloidal system ?

(*b*) What is the function of a colloidal system ?

14.21. Describe the phenomenon of Brownian movement seen in colloidal systems. What is its relationship to the stability of the dispersed particles of a colloidal system ?

14.22. (*a*) Explain the meaning of reversible and irreversible colloidal systems.

(b) Distinguish between peptization and condensation with proper illustrations.

14.23. What is a peptizing agent ? Is it always necessary for peptization ? Explain.

14.24. Write short notes on : (*a*) Electrophoresis. (*b*) Tyndall effect, (c) Emulsions, and (*d*) Hardy-Schultze rule.

14.25. Define the following terms : (*a*) Gold number, (*b*) Emulsification, (*c*) Demulsification, (*d*) Precipitation powers, and (*e*) Desorption.

14.26. (*a*) How does a dialysis membrane differ from an osmotic membrane and a filter paper ?

(*b*) List the various characteristics of colloidal solutions. Do they show colligative properties effectively ?

14.27. Discuss two methods for coagulating colloidal dispersions. Give their comparable merits and demerits.

14.28. (*a*) What is dialysis ? What are its uses ?

(*b*) What do you understand by the term 'electrophoresis' ?

14.29. What are micelles ? Give an example of a micellar system ?

14.30. (*a*) What are emulsions ? Give an example of an emulsion.

(*b*) Name the 'state' of the following substances : milk, collodion, cheese, butter, gum.

14.31. What is the role of adsorption in catalytic reactions ?

14.32. Give two examples of heterogeneous and homogeneous catalytic reactions.

14.33. Explain the meaning of 'activity' and 'selectivity' of catalysts ?

14.34. (*a*) What are zeolites ? Describe some of their features.

(*b*) What is shape-selective catalysis ?

14.35. (*a*) For a given reaction, what is the effect of a catalyst on (*i*) ΔH, (*ii*) the enthalpy of the products, and (*iii*) E_a ?

(*b*) Sketch the energy profiles for the catalyzed and uncatalyzed reactions

ANSWERS TO SELF ASSESSMENT QUESTIONS

14.1. (*i*) (*b*) (*ii*) (*b*) (*iii*) (*c*) (*iv*) (*a*) (*v*) (*d* (*vi*) (*b*) (*vii*) (*d*) (*viii*) (*a*) (*ix*) (*c*) (*x*) (*d*).

14.2. (*i*) dispersed phase and dispersion medium both as liquids.
(*ii*) size of colloide particles.
(*iii*) inversely proportional to temperature.
(*iv*) lower activation energy.
(*v*) adsorption.
(*vi*) surface area, adsorbing.
(*vii*) exothermic, enthalpy
(*viii*) adsorbents
(*ix*) reversible.
(*x*) higher ; lower

14.3. (*i*) T (*ii*) T (*iii*) F (*iv*) T (*v*) F (*vi*) F (*vii*) F (*viii*) F (*ix*) T (*x*) T

14.4. (*i*) 2 (*ii*) 1 (*iii*) 8 (*iv*) 7 (*v*) 9 (*vi*) 5 (*vii*) 6 (*viii*) 3 (*ix*) 4.

14.5. (*i*) The path of light becomes visible as the colloidal particles scatter light. This is called Tyndal effect.
(*ii*) $Fe(OH)_3$ sol is readily coagulated.
(*iii*) The electrically charged colloidal particles move towards electrodes when electricity is passed through the dispersions. The particles are discharged an electrodes and are coagulated.
(*iv*) Gelatin stabilizes the gold sol.
(*v*) Two oppositely charged sols on mixing in appropriate proportions lose their charge and become neutral. As a result, the colloidal particles of both the sols coagulate and settle down.

14.6. Sol is a colloidal solution in which solid is the dispersed phase and liquid is the dispersion medium, *e.g.* As_2S_3 sol. In an emulsion, both the dispersed phase and dispersion medium are liquids.

14.7. (*i*) Frictional clarification is caused by mutual rubbing of particles with molecules of dispersing phase. This sort of friction appears to be responsible for the charges over particles.
(*ii*) Electron Capture. At times particles capture electrons from air and during electrodispersion method (Bredigs' arc method).
(*iii*) Preferential adsorption of ions common to the particles from the solution phase.
(*iv*) Dissociation of surface molecules.
(*v*) Dissociation of molecular electrolytes adsorbed on the surface of particles.

14.8. All the particles in a particular colloidal dispersion carry the same charge, so the particles repel one another and do not coalesce into particles large enough to precipitate from the suspension.

14.9. This is because dialysis helps in removing undesirable ions from a colloidal preparation in order to stabilize the colloid.

14.10. A catalyst increases the rate of a reaction by providing an alternate pathway with a lower energy requirement (lower activation energy).

□ □

UNIT 15

Synthetic and Natural Polymers

Research is to see what everyone else has seen and to think what no one else has thought. —*ALBERT SZENT GYORGYI*

UNIT PREVIEW

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Explain the meaning of the terms : monomer, polymer and polymerization—addition and condensation.
2. Distinguish between the natural and synthetic materials.
3. Classify the polymers on the basis of their synthesis and physical behaviours.
4. Correlate the strength of polymers with the molecular forces present in them.
5. Explain the process of chain growth polymerizations and step growth polymerization.
6. Comment on the natural (unvulcanized), vulcanized and synthetic rubbers.
7. Give the names of natural and man made materials used as fibres.
8. Describe the synthesis, properties and uses of some important polymers.
9. Give the meaning of the terms : resins, plastics, polyesters, polyamide, *etc.*
10. Give the trade names of certain synthetic polymers.

15.1. INTRODUCTION

Polymers abound in today's world, both in nature and as products of modern technology. Plants, trees, bacteria, fish, birds, mammals and living systems all contain big molecules or polymers (Greek 'poly', many and 'meros' units). Some examples of naturally occurring polymeric substances are hair, silk, cellulose, starch, wool, diamond, graphite, rubber *etc*. We are also familiar with many synthetic polymers., *e.g.*, textile fibres like terylene, nylon, polyester, and various plastic materials like PVC, polyethene, polystyrene *etc.*

The situation in polymer chemistry changes almost overnight. It is not surprising that many scientists find this the most exciting area of scientific research.

Polymers are very large **molecules** that are formed by the combination of a very large number of relatively small molecules called **monomers**.

The individual large polymer molecules are known as macromolecules. The simplest form of polymer molecules are long chains composed of one type of repeating structural unit. There are also many natural polymers, often called '**biopolymers**', such as carbohydrates and proteins that often contain many different monomer units. Most of the synthetic polymers contain one type of monomer unit, *e.g.*, polyethylene $(CH_2)_n$. Nylon is a polymer formed from two different monomers.

Polymers vary widely in physical properties such as strength, flexibility and softening temperature. Some, such as polyesters, are very strong and not readily stretched and are, therefore, suitable for use as **fibres**, others, such as polyethene, are more easily deformed and are classed as **plastics**.

Polymers may be made from both inorganic and organic molecules. We have already discussed a number of inorganic polymers such as condensed phosphates, $(SO_3)_n$ silicates and silicones (Units 2 and 10). Most of the polymers, familiar to almost everybody are organic molecules and any synthetic in nature. Polymers may have various forms, *i.e.*, chains like polyethylene ; sheets like talc and mica ; and three dimensional giant molecules like quartz. But most synthetic polymers are chain like.

Nowadays, the materials made of polymers find varied uses starting from common household utensils, automobiles, clothes, furniture, *etc.*, to space aircraft and biomedical and surgical operations. Polymers are used as coatings such as paints, lacquers, and protective films and in adhesives. The field of polymer has now become an important field of study. Polymer chemistry has developed into a distinct and separate branch of chemistry. The German chemist Karl Ziegler (1893-1973) and Italian chemist Giulio Natta (1903-1979) shared the Nobel Prize for chemistry in 1963 for their work on polymerization. In this unit, we shall limit our discussion to organic synthetic polymers.

15.2. POLYMERS AND POLYMERIZATIONS

Polymers are molecules with high molar mass. Generally they have repeating units of the monomer. Since it would be impossible to write out the structure of a polymer, the repeating unit is put in parentheses along with a subscript *n* to indicate that the monomer is being repeated many times. Eventually the chain is terminated by

one of the several freak reactions. As a result, a polymer sample contains chains of varying lengths and, therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as proteins, contain chains of identical length and hence their molecular masses are singular in nature. The process by which monomers are transformed into a polymer is called **polymerization**. If there are more than one monomers from which a polymer (copolymer) is produced, then the process is called **co-polymerization**. Buna S rubber is a copolymer of butadiene and styrene. Buna N rubber is a copolymer of butadiene and acrylonitrile.

For example, polyethylene is obtained from its monomer ethylene as a result of polymerization. Here repeat unit is derived from the monomer ethylene.

$$\underset{\text{Ethylene}}{n\,CH_2{=}CH_2} \longrightarrow \underset{\text{Polyethylene}}{(CH_2{-}CH_2)_n}$$

Product formed from small number of monomers are called **oligomers**.

For example, if X is a monomer molecule then the short chain polymer like X—X and X—X—X, *etc.*, are oligomers.

X	monomer
X—X	dimer
X—X—X	trimer
X—X—X—X	tetramer
X—X—X—X—X	pentamer
n X	X ... $(X)_{n-2}$ ... X Polymer

The properties of polymers are, of course, dependent on the nature of molecular chains. Polymers may be linear, branched chain or have three-dimensional network structures (Fig. 15·1). The network polymers are also known as cross-linked polymers. **Linear polymers** are well packed and hence possess high densities, tensile strength and melting points *e.g.*, high density polyethene. Strength and melting point increase with chain length. **Branched chain polymers** are irregularly packed and hence tend to assume lower tensile strength and melting point than the linear polymers, *e.g.*, low density polyethene. Polymers with extensive **cross-linking** are hard, rigid and brittle, *e.g.*, bakelite.

(a)

(*a*) Linear polymers are well packed. They have high tensile strength, high melting point and high density. For example, high density polyethene.

(b)

(*b*) Branched chain polymers are not well packed. They have low density, low tensile strength and low melting point. For example, low density polyethene.

(c)

(*c*) Polymers with many cross-links (or net work polymers) are rigid, hard and brittle. For example bakelite.

Fig. 15.1. Patterns of chains in polymers

15.3. CLASSIFICATION OF POLYMERS

The word polymer includes compounds of diverse nature. They are classified by several different ways ; according to their occurrence, type of reaction by which they are prepared, their uses, nature of forces holding various molecules, their physical properties, *etc.*

Reference has already been made to natural and synthetic polymers.

Natural polymers include proteins, polysaccharides (starch and cellulose, *etc.*), silk, wool, skin, rubber, gums, resins, RNA, DNA *etc.* Starch is a polymer of glucose. It is generally represented by the formula $(C_6H_{10}O_5)_n$. The magnitude of n is such that the molecular mass is large, from 15000 to 100000. Cellulose is also a polymer of glucose. It is made by plants from glucose produced during photosynthesis. It has the same molecular formula as starch but its properties are very different. It is the principal constituent of all plant fibre. Cotton and wood are the principal sources of cellulose. Simi-

larly, protein is obtained as a result of polymerization of amino-acids. Protein, a long-chain polymer, sometimes cross-linked, contains 20-1000 amino-acids in a well defined arrangement. These biopolymers will be discussed in Unit 16. Natural rubber is a straight chain polymer of isoprene (2-methyl-1, 3-butadiene) units.

$$\underset{\text{Isoprene}}{n\mathrm{CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH{=}CH_2}} \xrightarrow{\text{Polymerization}} \underset{\text{Polyisoprene}}{\mathrm{(CH_2{-}\underset{\substack{|\\ CH_3}}{C}{=}CH{-}CH_2)_n}}$$

There may be 11,000 to 20000 isoprene units in the polymer chain of natural rubber.

Synthetic polymers, such as synthetic fibres (terylene, nylon), synthetic rubber, polyethylene, plastics, *etc.*, are usually cheaper than natural materials and are often better suited to their particular function since we are now able to produce a polymer to suit our specifications. They are said to be non-biodegradable as they cannot be broken down by the enzymes in bacteria. Their disposal presents a considerable problems as they cannot be economically recycled.

15.3.1. Classification Based on Synthesis

In the preparation of synthetic polymers, two modes of polymerization are used: addition polymerization and condensation polymerization. Based on these modes of synthesis, the macromolecules have been classified into two main groups: **addition polymers and condensation polymers.**

Addition polymerization and addition polymers

Addition polymers are built up by the repeated addition of monomers to the polymer chain. Molecules containing double bonds are particularly useful monomers as they can usually be made to undergo addition reactions among themselves. Addition polymers have the same empirical formula as their monomers. For example, mutual addition to ethene in the presence of a catalyst gives polyethene.

$$\underset{\substack{\text{Ethene}\\ \text{(Monomer)}}}{n\,\mathrm{CH_2{=}CH_2}} + \text{Acid catalyst} \xrightarrow[\text{and temperature}]{\text{High pressure}} \underset{\substack{\text{Polyethene}\\ \text{(Polymer)}}}{-\mathrm{(CH_2{-}CH_2)_n}}$$

Similarly propene (propylene) gives an addition polymer called polypropylene). Table 15.1 gives names, formulae and repeating units in common addition polymers.

$$\underset{\text{Propylene}}{n\,\mathrm{CH_3{-}CH{=}CH_2}} \longrightarrow \underset{\text{Polypropylene}}{-\mathrm{(CH_2{-}\underset{\substack{|\\ CH_3}}{CH})_n}-}$$

TABLE 15·1. Some common addition polymers and their uses

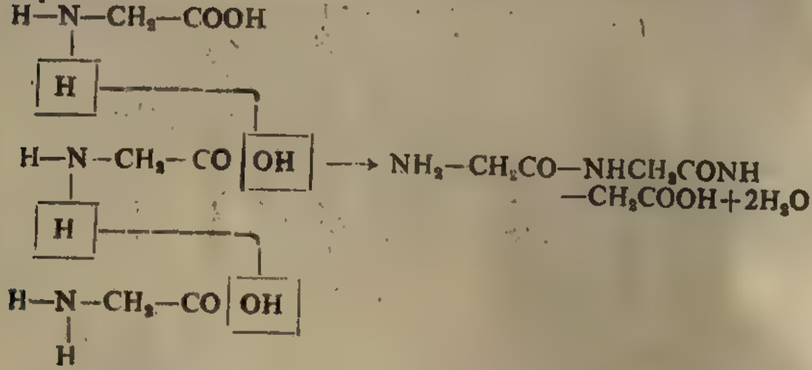
Monomer name, Structure	*Polymer name (Trade name)*	*Repeating unit, Structure*	*Uses*
Ethene $CH_2{=}CH_2$	Polyethylene or polyethene (Marlex Polyfilm)	$-(CH_2-CH_2)_n-$	Containers, pipes, bags, toys, electrical wire insulation, floor covering packing film, *etc.*
Propene $CH_2{=}CH$ $\vert$ CH_3	Polypropylene (Herculon)	$-(CH_2-CH)_n-$ $\vert$ CH_3	Fibres for ropes, carpets artificial turf, fishing nets, *etc.*; piper, moulded auto und appliances parts.
Chloroethene (Vinyl chloride) $CH_2{=}CH$ $\vert$ Cl	Polyvinylchloride or PVC (Tygon)	$-(CH_2-CH)_n-$ $\vert$ Cl	Wire and cable coverings, pipes, garden hoses, rainwear, shower curtains, floor tiles, plumbing, records, packing, films, toys, *etc.*
Cyanoethene (Acrylonitrile) $CH_2{=}CH$ $\vert$ CN	Polyacrylonitrile (Orlon ; Acrilan)	$-(CH_2-CH)_n-$ $\vert$ CN	Fibres for clothing, carpeting, upholstery, *etc.* Used as wood substitutes.
Vinyl acetate (Ethanoxyethene) $CH_2{=}CH$ $\vert$ $O.COCH_3$	Polyvinyl acetate or PVA	$-(CH_2-CH)_n-$ $\vert$ $OCOCH_3$	Emulsion paints, adhesives, lacquers *etd.*, protective films.
Vinyl alcohol $CH_2{=}CH$ $\vert$ OH	Polyvinyl alcohol	$-(CH_2-CH)_n-$ $\vert$ OH	Water soluble, thickening agents, used in cosmetics ; temporary protective films for metals.

Monomer name, Structure	*Polymer name (Trade name)*	*Repeating unit, Structure*	*Uses*
Methylmethaczylate $CH_2{-}\overset{\overset{\large CH_3}{\vert}}{\underset{\underset{\large COOCH_3}{\vert}}{C}}$	Polymethylmethacrylate (Plexiglas ; Luctile)	$-(CH_2{-}\overset{\overset{\large CH_3}{\vert}}{\underset{\underset{\large COOCH_3}{\vert}}{C}})_n-$	Glass substitute, lenses, aircraft glass, dental fillings, artificial eyes, braces, window panes and baths, windshields, *etc.*
Tetrafluoroethylene $CF_2{=}CF_2$	Polytetrafluoroethylene (Teflon ; Halon)	$-(CF_2{-}CF_2)_n-$	Gaskets, valves, tubing. coatings for cookware, storage containers, pipe sealing tape, *etc.*
Styrene $CH_2{=}\underset{\underset{\large C_6H_5}{\vert}}{CH}$	Polystyrene (Styrofoam ; Styron)	$-(CH_2{-}\underset{\underset{\large C_6H_5}{\vert}}{CH})_n-$	Moulded objects (combs, toys, brushes, cups, *etc.* refrigerator parts, insulating material, phonograph records, radio cabinets, *etc.*
1, 3 Butadiene $CH_2{=}CH{-}CH{=}CH_2$	Buna rubber	$-(CH_2{-}CH{=}CH{-}CH_2)_n-$	Tyres, rubber pipes, *etc.*
Isoprene (2-Methyl-1, 3-butadiene) $CH_2{=}\overset{\overset{\large CH_3}{\vert}}{C}{-}CH{=}CH_2$	Natural rubber	$-(CH_2{-}\overset{\overset{\large CH_3}{\vert}}{C}{=}CH{-}CH_2)_n-$	Toys, sport goods, adhesives, *etc.*

Condensation polymerization and condensation polymers.

Condensation polymers are formed by elimination of small molecules (usually water, alcohol, ammonia, *etc.*) during polymerization of monomers. Participating monomers normally contain two functional groups. One functional group of one monomer molecule reacts with the other functional group of the other monomer molecule. It gives a product with a functional group and the process of polymerisation continues. Some of these polymers are resins like urea-formaldehyde resin, phenol-formaldehyde resin (also known as bakelite). Common fibres like terylene, nylon and polyester also belong to this class.

Proteins, the condensation polymers, are made up of a series of amino acids (contains two functional groups, *i.e.*, amino group, $-NH_2$ and carboxylic group, $-COOH$) linked together in a unique sequence.



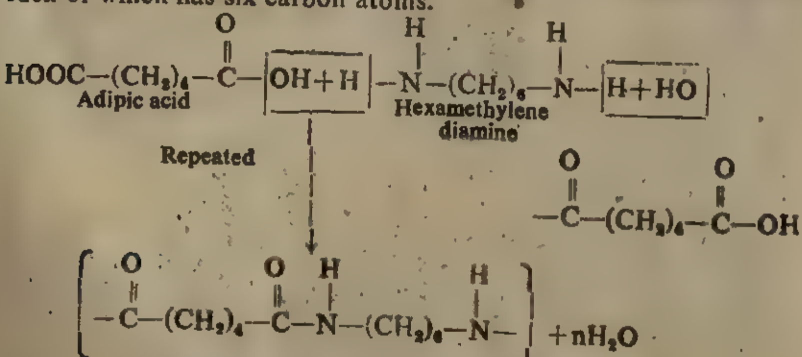
and so on.

$$nH_2N-CH_2COOH \longrightarrow (n-1)H_2O + H_2N-(CONH)_{n-1}COOH$$

Monomer — Polymer

Nylon 66 is produced by condensation reaction between hexamethylene diamine and adipic acid, a dicarboxylic acid.

It is so named because it is prepared from starting materials each of which has six carbon atoms.



Repeating unit of Nylon 66 (a polyamide)

TABLE 15.2. Some common condensation polymers, monomers and their uses.

Monomer name, Structure	*Polymer name*	*Repeating unit*	*Uses*
$HO—CH_2—CH_2—OH$ 1,2-Ethanediol (Ethylene glycol) + $CO_2H—(CH_2)_4—CO_2H$ Hexanedioic acid (Adipic acid)	Dacron (Mylar) a polyester	$—(O—(CH_2)_2—O—\underset{\underset{O}{\parallel}}{C}—(CH_2)_4—\underset{\underset{O}{\parallel}}{C})_n—$ Ester	Fabrics for seat beets and sails.
$NH_2—(CH_2)_6—NH_2$ 1, 6-Diaminohexane (Hexamethylenediamine) + $CO_2H—(CH_2)_4—CO_2H$ 1, 6-Hexanedioic acid (Adipic acid)	Nylon 66	$—(NH—(CH_2)_6—NH—\underset{\underset{O}{\parallel}}{C}—(CH_2)_4—\underset{\underset{O}{\parallel}}{C}—)_n$ Amide	The strength of nylon thread makes it suitable for use in making climbing ropes, tufted carpets, strings, fishing nets, parachute fabric, cords, tennis rackets, *etc*. It is also used for making amongst other things, curtain rail fitings, cupboard hinges, machine gear wheels and bearings, hosiery and other clothings, bristles for tooth brushes, surgical sutures, tyre cords and many other things.

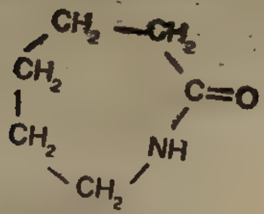
Monomer name, Structure	Polymer name	Repeating unit	Uses
 Azacyloheptan-2-one (γ-caprolactam)	Nylon 6	$-(\overset{O}{\overset{\|}{C}}-(CH_2)_5-NH)_n-$	Nylon is tough and has high tensile strength. It is used as a fibre in textile industry, *e.g.*, in elastic hosiery. It is also used for making bristles for brushes, in automobile tyres and many other things.
$HO(CH_2)_2-OH$ 1, 2-Ehtanediol (Ethylene glycol) + $COOH-C_6H_4-COOH$ 1, 4-Benzene dicarboxylic acid) (Terephthalic acid)	Tarylene or terene also Dacron ; a polyester	$(-O-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-)_n$	Fabrics in sails of boats, hose pipes, in magnetic recording tapes.
$C_6H_4(CO)_2O$ Phthalic anhydride + $\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$ Glycerol	Glyptal, a polyester		Linoleum, hard glass paint, *etc.* Phenograph records, combs, *etc.*
C_6H_5CHO Phenol + HCHO Formaldehyde	Bakelite		Electrical appliances, moulded cases of instruments.

Table 15.2 gives names, formulae and repeating units in common condensation polymers.

At times, we use the terms like chain growth and step growth polymers. In **chain growth polymerization**, monomers are added in a chain fashion. The chain growth is initiated by introducing a reactive free radical usually provided by thermal decomposition of organic peroxide, R—O—O—R to give two free radicals, R—O˙.

$$R-O^{\cdot}+CH_2=CH_2 \longrightarrow R-O-CH_2-CH_2^{\cdot}$$

The product is a free radical which, in turn, joins with another ethene molecule producing a free radical again.

$$R-O-CH_2-CH_2^{\cdot}+CH_2=CH_2 \rightarrow R-O-CH_2-CH_2-CH_2-CH_2^{\cdot}$$

and so on. The chain continues to grow until a termination reaction occurs.

In **step growth polymerization**, condensation occurs in steps with or without elimination of smaller melecules. The polymers already discussed can be grouped as chain growth and step growth polymers as suggested below :

Polymer involving chain growth polymerization

Polymer	*Monomer*
Polyethylene	Ethylene
Polypropylene	Propylene
Polybutadiene	Butadiene
Polyterafluoroethylene (Teflon or PTFE)	Tetrafluoro ethylene
Polyvinyl chloride (PVC)	Vinyl chloride

Polymers involving chain growth polymerization

Polymer	*Monomer*
Nylon-66	Adipic acid and hexamethylene diamine
Bakelite	Phenol and formaldehyde
Polyester (Terylene)	Terephthalic acid and ethylene glycol

15.3.2. Classification Based on Physical Behaviour

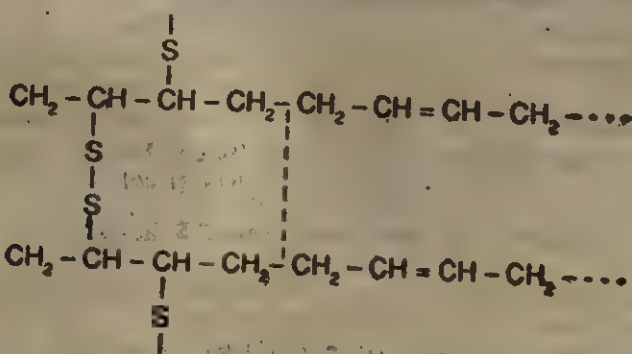
Polymeric materials may be classified according to their physical behaviour into the following classes:

1. Elastomers—possess the property of elasticity.
2. Fibres—possess high tensile strength and high modulus.
3. Thermoplastics—soften and become fluid on heating and may therefore be moulded.
4. Thermosetting—hard, influsible solids that are insoluble.

The physical behaviour of polymers limits their uses. Their uses originate from their unique mechanical properties like tensile strength, elasticity, toughness, *etc.* These mechanical properties depend upon intermolecular forces like van der Waals forces and hydrogen bonds operating in the macromolecules. There are many opportunities for such large molecules to become entangled through intermolecular forces. Apparently, longer the chain, more intense is the effect of intermolecular forces.

The infusibility of polymers mainly depends on the presence and the number of 'crosslinks' that join adjacent chains. These 'cross-links' shape the polymer into a frame work whose rigidity depends upon the degree of cross-links. The degree of cross-linking in molecular chains determines the most of the mechanical properties. The degree of intermolecular forces mainly depends upon the nature of the monomer units in the chain. For example, the attractive forces between molecular chains of polyethene would at best be rather weak compared to the hydrogen bonding between molecular chains of nylon. The tensile strength of high density polyethene (strong and extensive attractions between parailel chains) is almost three times as large as that of low density polyethene (weaker van der Waals attractions between parallel chains).

Elastomers : In elastomers, the molecular chains are joined by the weak intermolecular forces. These weak forces permit the polymer to be stretched. A few cross-links and relatively short chains are present in these polymers, which help them to restore its original form after stress is removed. Such polymeas are elastic in nature. Example vulcanized rubber. In vulcanization of rubber, the sulphur atoms react chemically with the linear molecules of rubber at some of their double bonds to cross link them (Fig. 15.2). The cross-linking is shown in butadiene rubber.



Cross - links through sulphur in vulcanized rubber

In this process the plasticity of rubber decreases but the elasticity is retained. When the vulcanized rubber is stretched, the chains

straighten out to some extent. When the tension on the rubber is released, the chains tend to coil up again. These chains cannot slip over one another because of polysulphide links.

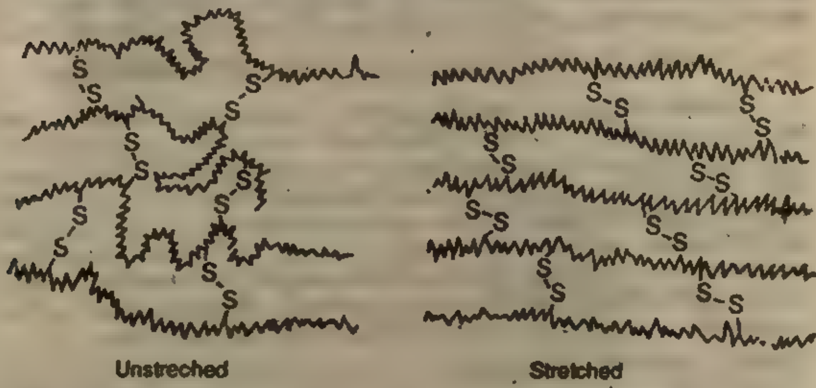


Fig. 15.2. Vulcanized rubber. The sulphur-sulphur crosslinks between the hydrocarbon chains. Such cross-links help rubber in regaining its original shape when stress is removed.

Vulcanized rubber has greater tensile strength and is water resistant. It is good for the manufacture of rubber bands, gloves and rubber tubing. It is unfit, because of its soft nature, for conveyor belts and motor tyres.

Fibres. Polymers with very high tensile strength and big molecules are used as fibres.

This is due to the strong intermolecular forces like hydrogen bonding operating between parallel chains for example, in polyamides (nylon-66). Such strong forces when present extensively, lead to close packing of chains and impart crystalline nature. These polymers, therefore, show sharp melting points and assume high tensile strength.

Thermoplastics. In thermoplastics, intermolecular forces of attraction are intermediate to those of elastomers and fibres. The characteristics of these plastics is that they became soft when heated under pressure and can then be moulded and remoulded. They are linear polymers and possess no cross-links between different chains. Some commonly used thermoplastics are polyethene, PVC, polystryene, *etc*. Many of the thermoplastics are formed by the polymerization of monomers which contain a C=C bond.

Thermosetting plastics. Such plastics contain three-dimensional networks of bonds and are moulded during the polymerization stage of their manufacture. They cannot be remoulded. The process of thermosetting is reversible while the process of thermoplastic

is reversible. Thermosetting plastics are normally made from relatively low molecular mass semi-fluid polymers. On heating under pressure in a mould these become infusible and form an insoluble hard mass. The infusibility of polymers mainly depends upon the presence and number of 'cross-links that join adjacent chains. Bakelite and glyptal resins belong to this class of polymers.

15.4. SOME COMMERCIALLY IMPORTANT POLYMERS

About 80% of the world's output of organic chemicals is used to make polymers. The use of polymers is not new : wood, cotton, wool and rubber are all naturally occurring polymeric materials. Today various types of synthetic polymers are known. A great advance in plastics technology has been made following the introduction of the Ziegler catalysts. Synthetic polymers are steadily replacing traditional natural materials. Man made polymers are usually cheaper and are often better suited to their particular function since now it is possible to produce a polymer to suit most specifications.

15.4.1. Addition Polymers

1. Polyolefins

Such polymers are produced from unsaturated hydrocarbons, *e.g.*, ethene, propene, styrene, *etc.*

(*i*) **Polyethene (polyethylene)** $(-CH_2-CH_2-)_n$

As the name suggests the monomer is ethylene. It was discovered in the early 1930's. Two varieties are made; 'low density polythene' and 'high density polyethene'. It is a thermoplastic. Polyethene is chemically inert to most substances; even to oxidizing acids and halogenated hydrocarbons. Polyethylene is a whitish, translucent polymer of moderate strength and high toughness. It is used as packing films and for making containers, pipes buckets, articles, electrical insulators, *etc.*

Low density polyethylene (density 0.091–0.094) is made by compressing ethylene under very high pressure at about 473 K, in mould the presence of a very small amount of oxygen.

$$nCH_2{=}CH_2 \xrightarrow[473K,\ 1500-2000\ atm]{O_2\ as\ catalyst} -(CH_2-CH_2)_n-$$

This variety softens at comparatively low temperature (393 K). It is a highly branched polymer with low density. High density polyethylene (0.95—0.97) is made be passing ethylene at 330–470K under pressure (6—7 atm) into an inert solvent (an aromatic hydrocarbon) containing a Ziegler catalyst (triethyi aluminium and titanium (IV) chloride). This material has a greater rigidity and higher softening point than the low density polymer. It is a linear

polymer with few branched chains. High density polyethylene can also be produced by polymerizing ethylene at a temperature 330K—470K and at 35 atm pressure in the presence of a catalyst, *i.e.*, chromium oxide supported over silica or alumina.

(*ii*) **Polypropylene** $(-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-)_n$

It is manufactured by passing propene under pressure into an inert solvent (heptane) containing a Ziegler catalyst, $(Al(C_2H_5)_3$ and $TiCl_4$.)

$$nCH_2-CH=CH_2 \xrightarrow[373\text{ K, }10\text{ atm}]{Al(C_2H_5)_3+TiCl_4} (-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-)_n$$

The polymer produced by this method contains the methyl groups (with same orientation) on the alternate carbon atoms (Fig. 15.3).

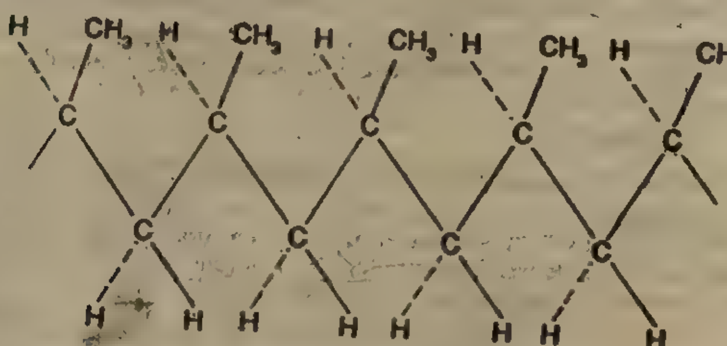


Fig. 15.3. A molecular mode of polypropene, an isotactic polymer.

This regularity in the arrangement of side chains leads to a closely packed structure (a crystalline) structure). Such polymers are described as **isotactic**. In atactic polymers, the side chains are oriented randomly. Such polymers are non-crystalline.

Polypropene is much harder, stronger and lighter than polyethene. It has the advantage of having a higher softening point. Its high tensile strength makes it suitable to produce tough fibres, used to make ropes and carpets. It is used in packing of textiles and foods, liners for bags and heat shrinkable wraps for records and mouldings, *etc.* It often replaces metal and glass.

(*iii*) **Polystyrene** $(-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-)_n$

Phenylethene (styrene) is polymerized by a typical method used for a number of other monomers. Styrene is treated with an initiator which on decomposition gives free radicals. The free radical adds to the alkene forming a new radical which, in turn, adds to another molecule of styrene.

$$\underset{\text{Dibenzoyl peroxide}}{C_6H_5-CO-O-CO-C_6H_5} \xrightarrow{\text{Heat}} \underset{\text{Free radical } (R^{\cdot})}{2C_6H_5CO-O^{\cdot}}$$

$$R^{\cdot}+CH_2=\dot{C}H-C_6H_5 \longrightarrow R-CH_2-\dot{C}H-C_6H_5$$

$$R-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{C}H^{\cdot}}+CH_2=\underset{\displaystyle C_6H_5}{\underset{|}{C}H} \longrightarrow R-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{C}H}-CH_2-\underset{\displaystyle C_6C_5}{\underset{|}{C}H^{\cdot}}$$

The above process continues until the chain is interrupted and polymerization stopped.

Polystyrene, a linear polymer, is a thermoplastic. It is white, transparent and floats on water. It is used to make food containers, disposable cups, model construction kits, ceiling tiles, packing for delicate articles, lining material for refrigrators television bodies *etc.*

Polysyrene is sold under the name of styrofoam or styron. It is resistant to alkalis and halogen acids. Copolymers of butadiene and styrene resemble natural rubber (SBR).

2. Polydienes

Such polymers are produced from butadiene, chloroprene, *etc.*

(*i*) **Neoprene.** It is a synthetic elastomer with rubber like properties. It was first produced in 1931 by polymerization of chloroprene. Chloroprene is similar to isoprene except for the replacement of a methyl group by a chlorine atom.

$$\underset{\substack{\text{Isoprene}\\ \text{(2-Methylbuta}-1,3-\text{diene)}}}{CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2} \qquad \underset{\substack{\text{Chloroprene}\\ \text{(2-Chlorobuta}-1,3-\text{diene)}}}{CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2}$$

$$nCH_2=CH-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2 \xrightarrow{S_2O_8^{2-}\text{ as catalyst}} \underset{\text{Neoprene}}{(-CH_2-CH=\underset{\displaystyle Cl}{\underset{|}{C}}-CH_2-)_n}$$

The structure of neoprene is similar to that of natural rubber.

Properties of neoprene. (*i*) It is more elastic than natural rubber. (*ii*) It is non-inflammable while natural rubber can burn. Chlorine atoms present in neoprene make it non-inflammable. (*iii*) It possesses higher temperature resistance. It retains its usefulness over a wide range of temperature. (*iv*) It is more resistant to action of oils, gasoline and solvents than natural rubber. (*v*) It resists

abrasion well. It is stable towards sunlight and is not attacked by oxygen and ozone.

Uses of neoprene. (*i*) Neoprene, because of its resistance to action of oils, gasoline and solvents, is used for making gasoline and oil hose, automobile, aircraft and refrigerator parts and electrical insulation in motor engines *etc.* (*ii*) It is used for making conveyor belts used in coal mines because it will not catch fire. (*iii*) It is also used in the production of synthetic adhesives and rubber cement.

(*ii*) **Styrene-Butadiene Rubber (SBR).** This rubber is also known as Buna-S-Rubber. It is a copolymer of butadiene and styrene. The reaction is as follows :

$$\underset{\text{Butadiene}}{nCH_2=CH-CH=CH_2} + \underset{\text{Styrene}}{nCH_2=\underset{\displaystyle C_6H_5}{\underset{|}{CH}}} \xrightarrow{\text{Na catalyst}}$$

$$\underset{\text{Buna-S}}{(-CH_2-CH=CH-CH_2-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-)_n}$$

It is used for manufacturing toys, tyres, sport goods and adhesives.

Buna-S is similar to natural rubber. It is more difficult to plasticise, responds less to softening agents and is deficient in surface stickiness. As compared to natural rubber, it ages with less change in physical properties and its decomposition temperature is higher. But it shows heat brittleness and tends to crack on repeated bonding.

(*iii*) **Nitrile-Butadiene Rubber (NBR).** NBR is also known as Buta-N rubber. It is obtained by polymerizing butadiene and acrylonitrile. The polymerization reaction is :

$$\underset{\text{Butadiene}}{nCH_2=CH-CH=CH_2} + \underset{\text{Acrylonitrile}}{nCH_2=\overset{\displaystyle CN}{\overset{|}{CH}}} \longrightarrow$$

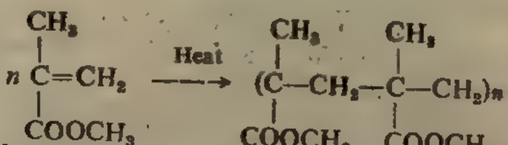
$$\underset{\text{NBR}}{\left[\ldots CH_2-CH=CH-CH_2-CH_2-\overset{\displaystyle CN}{\overset{|}{CH}}-\right]_n}$$

NBR resists the action of oils, gasoline and organic solvents. It is used as oil seals, in the manufacture of hoses and tank linings needed for handling and storage of solvents.

3. Polyacrylates

Polymers of this class are obtained from a variety of acrylic monomers and their derivatives.

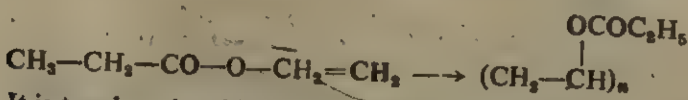
(*i*) **Polymethylmethacrylate (PMMA).** It is sold under various commercial names like **plexiglass, acrylite, perspex and lucite.**



Methyl 2-methylacrylate or Methyl-2-methyl propenoate — Polymethylmethacrylate

It is a hard transparent material with a glossy surface. It has good resistance to the effect of light and ageing. It is useful for lenses, transparent domes and skylights, dentures, aircraft windows and protective coatings, plastic jewellery, moulded novelties, sign-boards and for decoration purposes.

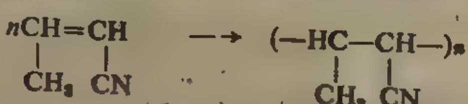
(*ii*) **Polyethylacrylate.** Ethenyl propanoate ($CH_2=CH-COOC_2H_2$) or ethyl acrylate is polymerized in the same way as styrene



It is tough and rubber like product. It forms an emulsion with water and this emulsion is the basis of plastic emulsion paint.

There is another product called polyvinyl acetate (polyethenyl ethanoate). It is an important constituent of plastic emulsion paint. It is used in 'chewing-gum base' and in solution in acetone to grease-proof paper.

(*iii*) **Polyacrylonitrile (polypropenonitrile).** It is a long chain polymer



Polyacrylonitrile

Its trade names are Acrilan, Orlon, or Courtille. It can be spun into long fibres which can be made curly like sheep's wool. Acrylic fibres are strong, have a good chemical resistance and are almost unaffected by sunlight. They are often used as blends, *e.g.* mixed acrylic-wool fabrics. Acrilan fibres are used for cloth, carpets and blankets.. It is also used in preparation of other polymers to improve their qualities.

4. Polyhalo-olefins

These polymers are derived from halosubstituted ethene monomers.

(*i*) **Polytetrafluoroethylene, or (Teflon or PTFE), $(F_2C-CF_2)_n$**

$$\underset{\text{Tetrafluoroethylene}}{nCF_2=CF_2} \xrightarrow{S_2O_8^{2-}\text{ as catalyst}} \underset{\text{Teflon}}{(-CF_2-CF_2-)_n}$$

Teflon resists the action of acids, alkalis and oxidizing agents. It is an extremely inert polymer and stable towards high temperature. It is a smooth, slippery and soft polymer. It possesses 'anti-stick' properties.

Because the C—F and C—C bonds are strong, it has a very high softening point (600 K). It has good electrical resistance and perhaps the best chemical resistance of any known material.

It is used in the manufacture of gaskets, seals, non-lubricated bearings, filtes clothes, *etc*. It is also used in non-stick pan coatings.

For making a teflon coated utensil, teflon powder is spread on the surface of the utensil, which is slowly heated to high temperature. This method is unsuitable for mass production, leading to high costs.

(*ii*) **Polymonochlorotrifluoroethylene (PCTFE)** $(ClFC-CF_2)_n$ It is similar in properties to PTFE. However, the presence of chlorine atoms causes this polymer to be less resistant to heat and to chemicals.

(*iii*) **Polyvinyl chloride**, or (PVC), $(-CH_2-\underset{\substack{|\\Cl}}{CH}-)_n$

It is a polymerized product of vinyl chloride. The monomer is converted into a polymeric product by heating in an inert solvent with dibenzoyl peroxide.

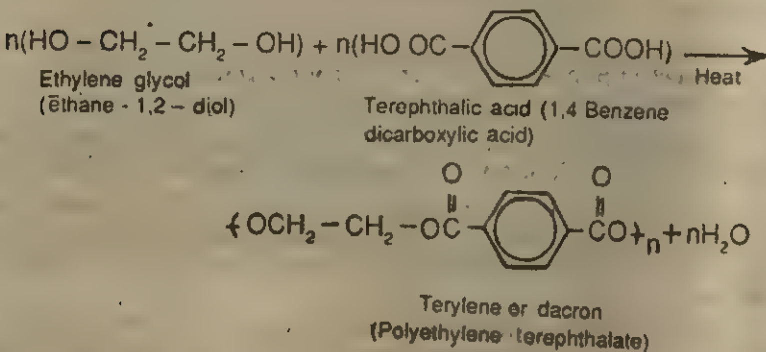
$$n\,CH_2=\underset{\substack{|\\Cl}}{CH} \longrightarrow (-CH_2-\underset{\substack{|\\Cl}}{CH}-)_n$$

It is a very tough polymer, and a plasticiser (benzene, 1, 2-dicarboxylic acid) is added to soften it. It has good chemical and electrical resistance and because of the presence of chlorine atoms has lower flammability than polyethene. It is used in the manufacture of artificial leather, household goods (curtains, table cloths, *etc*.) gramophone records and floor coverings. The flexible variety is used for wire and cable insulation, hose pipes and wrapping material (raincoats *etc*.). A co-polymer of vinyl chloride and vinyl acetate is suitablefor making floor titles and gramophone records.

15·4·2. Condensation Polymers

1. **Polyesters.** Polymers with ester linkages are termed as polyesters.

(*i*) **Terylene** is made by the condensation of the acid, benzene-1, 4-dicarboxylic acid (terephthalic acid or one of its derivatives, *i.e*, dimethyl terephthalate) with ethane—1, 2-diol (ethylene glycol) in the presence of a weak base such as calcium acetate. The polymer is also known as Dacron.



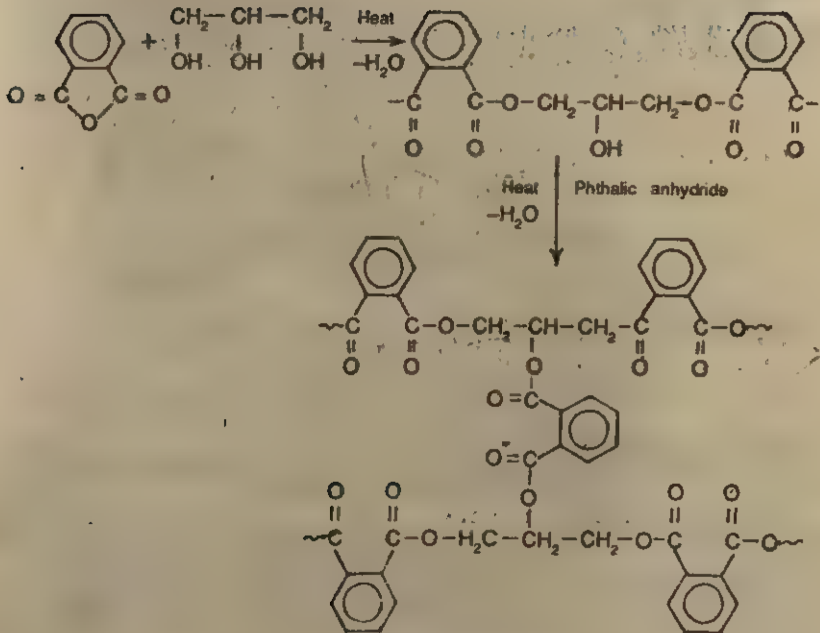
Terylene is tough, thermoplastic, and very resistant to action of chemical or biological substances and to abrasion. It has low moisture absobing power. Terylene forms strong fibres. It is used as a blend with cotton and wool in clothing.

Terylene clothes do not get crumped on washings and rough use, Their crease remain intact (crease resistant). This property has enhanced its use in the manufacture of textiles. Further, due to its high tensile strength and resistance to tearing, it is used for making magnetic recording tapes. Terylene is used for shaping the sails of boats. These sails are light and strong.

Aprons and other protecting clothings of terylene are used in industries and laboratories. These are resistant to action of chemical *etc.*

Terylene has found its use in the hoses used by firemen—as it is tough and quick in drying. Moreover, its hoses do not deteriorate when stored wet.

(*ii*) **Glyptal resin.** The glyptals are polyesters formed from propane, —1, 2, 3 triol (glycerol) and benzene —1, 2-dicarboxylic (phthalic) anhydride. This is a three-dimensional thermosetting polymer.



Glyptal, a polyester (alkydresin)
(Thermosetting)

A synthetic resin is the material from which plastic (a final and useful form) is made. Glpytal of ethylene glycol and phthalic acid is also known. They are used in the manufacture of paints and lacquers.

2. Polyamides

Polyamides are the polymers with amide linkages in the polymeric chain.

(*i*) **Nylon.** The name 'Nylon' is applied to certain synthetic polyamides. A number of these are known. The two most important ones are called Nylon 66 and Nylon 6.

Nylon 66. It is made by condensation of adipic acid and hexamethylene diamine :

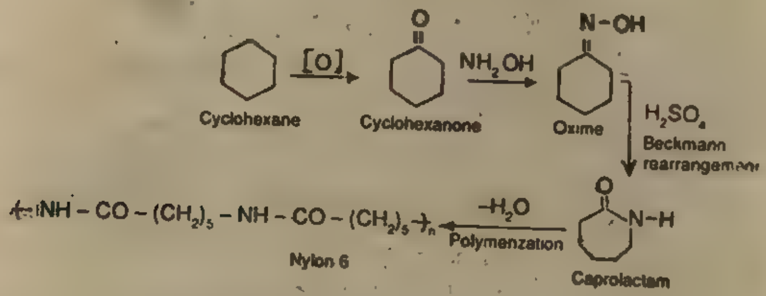
$$n\ H_2N\ (CH_2)_6\text{—}N\begin{smallmatrix} H \\ N \end{smallmatrix} + n \begin{smallmatrix} HO \\ O \end{smallmatrix}\!\!>\!C\text{—}(CH_2)_4\text{—}COOH$$

Hexamethylene diamine — Adipic acid

$$\text{—(—NH—}(CH_2)_6\text{—NH—CO—}(CH_2)_4\text{—CO—)}_n$$

The name is based on the fact that both the monomers contain six carbons each.

Nylon 6 This polymer is made up of only one type of monomer of six carbon atoms, namely caprolactam, which itself is made from cyclohexane (a petrochemical) as follows :



The step involving the conversion of cyclohexanone oxime into caprolactam is an example of Backmann rearrangement.

Nylons (polyamides) are the most useful and versatile of all the known fibres. Nylon was first made in 1935 by Wallace H. Carothers, the American chemist who also happens to be the first to make terylene. Structurally nylon and proteins are similar as both have amide linkage (—CO—NH—).

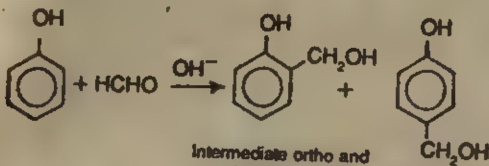
On cooling, the molten polymer is extended into ribbons which are cut into flakers and chips. The fibre is produced by remelting and extruding the molten polymer into thin filiaments, which are spun onto spools. During the melt-spinning process, the filament can be stretched to desired length to add strength. The strength is attributed by the increased cross-linkes in the polymer.

Nylon 66 makes extremely strong threads and fibres because its long chain molecules have stronger intermolecular forces. Fibres are extremely tough, resistant to friction and are chemically inert. It lacks the softness and moisture absorbing properties of the natural fibre. It is, however, harder wearing and has good 'wash and wear' characteristics. Nylon clothes become dry rapidly. It is popularly called 'drip-dry' property of nylon. Wool is blended with nylon to increase its strength and resistance against abrasion. Nylon imparts woollen garments a much longer life. Nylon 6 has many uses (Table 15·2).

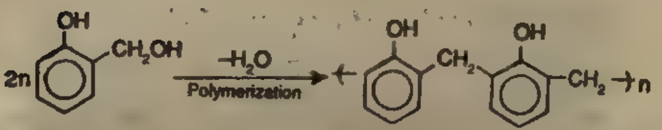
3. **Formaldehyde resins**. This class of polymers includes polymers like bakelite and melamine polymers.

(*i*) **Phenol-formaldehyde resin (Bakelite)**. This plastic, known for about a hundred years, is manufactured by heating phenol and formaldehyde (as formalin) in the presence of sulphuric acid. In the first stage a polymer without much cross linking, is produced. In the initial stage of reaction, both **ortho-** and **para-**

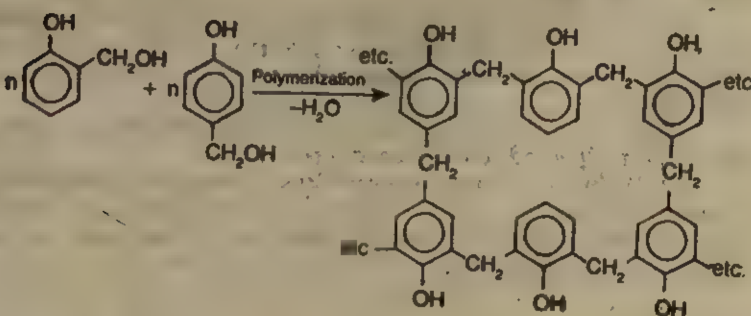
hydroxymethyl phenols are formed These phenols polymerize to give linear polymer and cross-linked copolymer (bakelite).



Intermediate ortho and para hydroxy methyl phenol



Linear polymer with methylene bridges



Cross- linked polymer bakelite

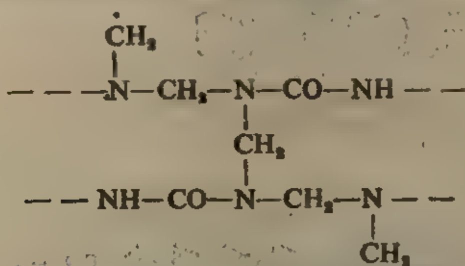
Cross-linked bakelite is a thermosetting polymer.

Bakelites with low degree of polymerization are soft in nature and are used in varnishes, lacquers and as a glue for laminated wooden planks and other products. Bakelites with high degree of polymerization are hard in nature and are used for making electrical goods, phonograph records, fountain pen barrels, combs, brake linings, foundary patterns, *etc.* Sulphonated bakelite polymers are used as ion-exchange resins.

(*ii*) **Urea formaldehyde resin.** Urea and formaldehyde (used as formalin) when heated together condense to form a polymer, which can be moulded into different shapes.

$$H_2C{=}O + H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 + O{=}CH_2 \longrightarrow --CH_2{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}CH_2--$$

on further heating some cross linking occurs,



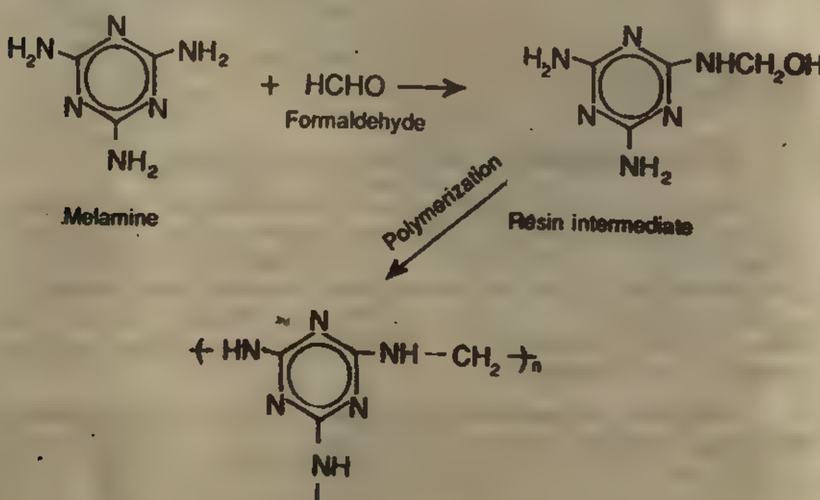
Polymerized resin

The polymerized resins are hard, chemically inhert and resist the attack of solvents. They are thermosetting and cannot be reshaped by heating.

Urea formaldehyde resin, like bakelite is hard but brittle. However, it has one advantage over bakelite, that since it is itself lacking in colour, products using this polymer can be given any colouration.

It is used for electrical insulation, making bottle caps, and as adhesives for plywood, block board, *etc.*

(*iii*) **Melamine formaldehyde resin.** Melamine and formaldehyde copolymerize producing a resin. This polymer is used in making plastic crockery--cups and plates *etc.* These cups *etc.* are hard and do not break easily.



Melamine polymer, a resin

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

15.1. Choose the correct answer of the four alternatives given for the following questions :

(*i*) Neoprene is a polymer of
- (*a*) isoprene
- (*b*) chloroprene
- (*c*) 1, 2-dichloroethane
- (*d*) butadiene.

(*ii*) Buna-S rubber is synthesized from
- (*a*) butadiene and styrene
- (*b*) butadiene and acrylonitrile
- (*c*) isobutylene and isoprene
- (*d*) 1, 2-dichloroethane and sodium polysulphide.

(*iii*) Which of the following is an artificial fibre ?
- (*a*) silk
- (*b*) wool
- (*c*) cotton
- (*d*) nylon

(*iv*) The raw material for making Nylon 6 is
- (*a*) Caprolactam
- (*b*) Butadiene
- (*c*) Adipic acid
- (*d*) Phthalic acid.

(*v*) Polyethene is a
- (*a*) Fluoro compound
- (*b*) Chloro compound
- (*c*) Nitrogen compound
- (*d*) Hydrocarbon.

(*vi*) Natural rubber is a polymer of
- (*a*) Ethylene
- (*b*) Butadiene
- (*c*) Isoprene
- (*d*) Styrene.

(*vii*) Nylon 66 is a co-polymer of
- (*a*) Phenol and formaldehyde
- (*b*) Phthalic acid and ethylene glycol
- (*c*) Phthalic acid and ethyl alcohol
- (*d*) Adipic acid and hexamethylene diamine.

(*viii*) Nylon is a
- (*a*) Polyester
- (*b*) Polyamide
- (*c*) Polyalcohol
- (*d*) Polymerized hydrocarbon.

(*ix*) Which of the following polymers are hard ?
- (*a*) thermoplastic
- (*b*) linear polymer
- (*c*) cross-linked chain
- (*d*) branched chain

(*x*) Which of the following is the thermoplastic ?
- (*a*) bakelite
- (*b*) glyptal
- (*c*) nylon
- (*d*) none

15.2. Fill in the blanks :

(*i*) The process of combining sulphur with rubber to improve its useful properties is called.........

(*ii*) Natural latex is a milky sap from a......tree.

(*iii*) ......and ......are examples of natural fibres.

(*iv*) Polymers are the molecules with......molar mass and have......of the monomer.

(v) Buna-N is a copolymer of butadiene and.......
(vi) Thermoplastics soften and become......on heating.
(vii) The infusibility of polymers mainly depends on the presence and number of......that join adjacent chains.
(viii) Tygon is a polymer of......
(ix) Oslon is a polymer of......
(x) Ziegler catalyst is a mixture of......and.......

15.3. Which of the following statements are true (T) and false (F) ?

(i) Terylene and dacron are the names of different products.
(ii) Natural rubber is a thermoplastic.
(iii) Monomers with more than two reactive centres grow in a three dimensional polymers which are usually hard and called thermosettings.
(iv) Teflon is a polymerized product of fluoroethylene.
(v) The degree of intermolecular forces mainly depends upon the nature of the monomer units in the chain.
(vi) Polyester and polyamide polymers are examples of addition polymers in which two types of monomer units are copolymerized.
(vii) Proteins are the copolymers of amino acids.
(viii) Linear polymers are not well packed and hence possess low densities.
(ix) Glucose is a polymer of cellulose.
(x) Marlex is the trade name of polypropylene.

SHORT ANSWER QUESTIONS

15.4. What is vulcanization ? How does the vulcanized rubber compare with the natural rubber ? What are the main uses of vulcanized natural rubber ?

15.5. Give reasons briefly for the following :

(i) Cotton and woollen dresses keep us warm in winter.
(ii) Cotton clothes keep us comfortable in hot weather.
(iii) Nylon is a suitable material for making climbing ropes.
(iv) Nylon has a dip-dry property.
(v) Wool is blended with nylon.

15.6. Why are cotton clothes being replaced by terylene clothes ?

15.7. Give the characteristics of nylon fibres.

15.8. Write down the uses of nylon fibres. What properties of nylon make it specially suitable for the purpose ?

15.9. What are the advantages when terylene is mixed with wool to prepare cloth ?

15.10. Name the starting materials used in the manufacture of Nylon 66 and terylene.

15.11. What is thermoplastic ?

15.12. What is the monomer of the following polymers :

(i) Starch (ii) PVC
(iii) Dacron (iv) Teflon.

TERMINAL QUESTIONS

15.1. Define the term polymerization.

15.2. What are polymers ? Discuss the various schemes for their classification.

15.3. Define the following terms :

(*i*) Thermoplastic (*ii*) Thermosetting
(*iii*) Elastomer.

15.4. Write the names and structures of the monomers of bakelite and glyptals. To which class, thermoplastic or thermosetting do bakelite and glyptals belong ? Give reasons.

15.5. What is the difference between the two notations : nylon-6 and nylon-66 ? How are nylon-6 and nylon-66 synthesized ? Give equations.

15.6. What is Buna-S ? How does it differ from natural rubber ? How is it synthesized ?

15.7. Write the equations for synthesis of
(*i*) Polymethylmethacrylate (*ii*) Polyacrylonitrile
(*iii*) Teflon (*iv*) PVC
(*v*) Glyptal (*vi*) Polystyrene.
Also give two important uses of each polymer.

15.8. Write the names and structures of the monomers associated with the following polymers :
(*i*) Natural rubber (*ii*) Nylon-66
(*iii*) Terylene (*iv*) Polymonochlorotrifluoroethylene
(*v*) Neoprene (*vi*) Cellulose
(*vii*) Proteins.

15.9 Explain the following terms with suitable examples :
(*i*) Natural polymers (*ii*) Synthetic polymers
(*iii*) Polyamides (*iv*) Polyesters
(*v*) Chain growth polymerization (*vi*) Step growth polymerization
(*vii*) Macromolecules (*viii*) Isotactic
(*ix*) Atactic. (*x*) Co-polymer

15.10. What are the structures of the polymers formed from the following monomers ?
(*i*) propene (*ii*) $CH_2{=}CH{-}CH{=}CH_2$
(*iii*) 1, 6, Hexanediamine and 1, 4, hexanedioic acid
(*iv*) 1, 2, Ethanediol and terephthalic acid.

15.11. What structural characteristic must be present in an organic molecule for it to undergo addition polymerization ?

15,12. Give the characteristics of linear, branched and cross-links polymers.

ANSWERS TO SELF ASSESSMENT QUESTIONS

15.1. (*i*) (*b*) (*ii*) (*a*) (*iii*) (*d*) (*iv*) (*a*) (*v*) (*d*) (*vi*) (*c*)
(*vii*) (*d*) (*viii*) (*b*) (*ix*) (*c*) (*x*) (*c*).

15.2. (*i*) vulcanization (*ii*) rubber
(*iii*) silk and wool (*iv*) high, repeating unit
(*v*) acrylonitrile (*vi*) fluid
(*vii*) cross-links (*viii*) chloroethene
(*ix*) acrylonitrile (*x*) triethyl aluminium and titanium chloride.

(IV)

15.3. (*i*) F (*ii*) T (*iii*) T (*iv*) F (*v*) T (*vi*) F (*vii*) T
(*viii*) F (*ix*) F (*x*) F

15.4. It is a process of heating natural rubber with sulphur. Vulcanized rubber is soft, has greater tensile strength and is water resistant. It is suitable for the manufacture of rubber bands, gloves and rubber tubing.

15.5. (*i*) Cotton and woollen dresses are bad conductor of heat, and hence, prevent the loss of body heat. Thus cotton and woollen dresses help us to keep warm.

(*ii*) Cotton dress material allow the sweat to pass through. This makes us comfortable in hot weather.

(*iii*) Because the nylon climbing ropes are very light, strong and flexible. They do not become stiff either at low temperatures or when wet.

(*iv*) Nylon clothes dry out very quickly as they have low degree of moisture absorption. This property of nylon is called 'drip-dry' property.

(*v*) Wool is blended with nylon to increase its strength and resistance against abrasion.

15.6. Cotton clothes shrink on washing, do not retain creases, are attacked by mildew and mould, and are highly inflammable. Terylene clothes are resistant to action by chemical or biological agents, and have low moisture absorbing property.

Further the creases set into terylene clothes are fast and long lasting because of its heat setting quality.

15.7. (*i*) Low degree of moisture absorption.

(*ii*) High degree of tensile strength.

15.8. (*i*) High degree of tensile strength of nylon is responsible for many of its uses. Heavy loads can be suspended from thin cords of nylon. Nylon is used for making fishing nets, parachute fabric, cords and climbing ropes.

(*ii*) Low degree of moisture absorption of nylon makes it to dry rapidly. Therefore it is used in the manufacture of socks. Its strength, flexibility and retention of original shape after use also make nylon useful for clothes *etc*.

15.9. Wool blended with terylene acquires strength and resistance against abrasions. Its life also increases. Terylene mixed wool is used for the manufacture of suitings.

15.10. Nylon 66 : Adipic acid and Hexamethylene diamine.

Terylene : Terephthalic acid or dimethyl terephthalate and ethylene glycol.

15.11. A variety of plastic which becomes soft on heating and acquires its original nature without undergoing much change in its physical and chemical properties. Such a plastic material can be repeatedly used by moulding into desired shapes.

15.12. (*i*) α-Glucose (*ii*) $CH_2{=}\underset{\underset{Cl}{|}}{CH}$

(*iii*) Ethylene glycol and terephthalic acid.

(*iv*) $CF_2{=}CF_2$

□ □

UNIT 16

Biomolecules : Structure and Function

...I cannot help wondering whether some day an enthusiastic scientist will christen his newborn twins—Adenine and Thymine.

—*F.H.C. CRICK*

UNIT PREVIEW

16.1. Introduction.

16.2. Carbohydrates : monosaccharides, disaccharides, polysaccharides.

16.3. Proteins : amino acids, peptide bond and structure of proteins, shape and biochemical functions of proteins, denaturation of proteins.

16.4. Enzymes.

16.5. Nucleic acids : nucleotides and nucleosides, structures of DNA and RNA, chemistry and heredity—replication, protein synthesis, the genetic code, mutation.

16.6. Lipids : fats and oils, phospholipids, cell membrane, steroid lipids.

16.7. Chemical evolution : origin of life

Self assessment questions.

Terminal questions.

Answers to self assessment questions.

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Give a definition of biochemistry and macromolecules.
2. Comment on living cell and its functions.
3. Describe the natural sources of carbohydrates and their chemical composition.
4. Classify and describe the various types of the carbohydrates.
5. Describe proteins and their major functions.
6. Describe and classify amino acids according to their side chains.
7. Comment on the various characteristics of amino acids.
8. Comment on the bonding and structure of peptide chain in the α-helix and beta pleated sheet.
9. Understand the meaning of the following terms associated with proteins : fibrous, globular, α-amino acid, asymmetric carbon atom, chiral centre, peptide bond, denaturation, primary, secondary and tertiary condensation.
10. Describe the importance of enzymes.
11. Describe the structures of nucleosides, nucleotides, and the DNA double helix.
12. Comment on the basic composition of nucleic acids.
13. Describe the important biological functions of nucleic acids.

14. Comment on the chemistry and heredity.
15. Discuss the causes of mutation and its consequences.
16. Describe the lipids and their functions.
17. Describe the chemical constituents of cell membrane and their importance.
18. Define the following terms : saponification, hydrogenation, replication, transcription, gene, triple, codon, anticodon, photosynthesis, fatty acids, specificity and selectivity.
19. Emphasize and understand the importance of the macromolecules for our living system.
20. Comment on the chemical evolution.

16 1. INTRODUCTION

Biochemistry is the science that deals with chemical processes and materials in living systems. The focal point of biochemistry and biochemical aspects of the chemicals is the cell, the basic building block of living systems where most life processes are carried out. Thus, from a chemical point of view, LIFE can be considered to be the set of complex reaction systems found in organisms which, by tradition, we call LIVING.

Many of the molecules found in living cells are structurally and functionally among the most complex organic substances known to mankind. Living organisms mainly consist of water, proteins, carbohydrates, lipids (fats and oils) nucleic acids and certain inorganic substances. Each component of the living system appears to have a specific purpose or function. To maintain and sustain the high degree of order, the living state requires the information of heredity, the energy of biochemical reactivity and sufficient raw materials to build cells.

The chemical reactions which take place in the course of synthesizing the organic molecules—micro and macro—are given a collective name '**metabolism**'. Two types of metabolisms are catabolism and anabolism. **Catabolism** relates to the breakdown of organic molecules, *e.g.*, breaking of sugar into carbon dioxide and the breakdown of amino acids to urea. Energy is released in the process. **Anabolism** relates to the building up of more complex structures from simple ones, *e.g.*, nitrogen is first converted to ammonia and then to complex organic nitrogen compounds, the formation of fatty acids from acetic acid and the formation of proteins from amino acids. All life processes—such basic functions as reproduction, growth, movement, thinking and ageing—depend on such chemical reactions.

Biosubstances, carbohydrates, proteins, lipids and nucleic acids are interwoven to make up the thread of life. In this unit, we shall study about these lifeless molecules and how these groups of substances interact with each other to constitute, maintain and perpetuate the living state.

16.2. CARBOHYDRATES

This class of compounds are among the most major constituents of most living systems ; act as the main source of energy for biological processes as well as a structural component in plants. In plants, they form the greater part of the cell tissue on which the plant relies for its support. They include familiar substances like glucose, sucrose, starch, cellulose, *etc.* They provide with all the three basic needs of life, *viz.*, food (as starch containing grains) clothing and shelter (cellulose in the form of cotton, linen, wood, *etc.*). The name originates from the fact that many sugars (which form parts of this class of compounds) have the general formula $C_n(H_2O)_m$—*i.e.*, carbon hydrate—hence the name carbohydrates. Thus, glucose, $C_6H_{12}O_6$ the most common sugar, can be written as $C_6(H_2C)_6$ and sucrose as $C_{12}(H_2O)_{11}$. However, these representations do not explain their relative nature. They bear little or no relationship to the structures known today.

They are produced by green plants (by chlorophyll, the green pigment of plants) in nature from carbon dioxide and water by the action of sunlight via a process called photosynthesis. Thus, carbohydrates are the end products of photosynthesis in plants.

$$nCO_2 + mH_2O + \text{solar energy} \longrightarrow \underset{\text{Carbohydrate}}{C_n(H_2O)_m} + nO_2$$

$$\text{or} \quad 6CO_2 + 6H_2O \underset{\substack{\text{Animal respiration} \\ \Delta H = -2860 \text{ kJ mol}^{-1}}}{\overset{\substack{\text{Plant photosynthesis} \\ h\nu \text{ (chlorophyll)}}}{\longleftarrow\!\!\!-\!\!\!-\!\!\!-\!\!\!-}} C_6H_{12}O_6 + 6O_2$$

The driving force for the reaction is supplied by sunlight. **This reaction helps in strong some of the energy given out by the sun.** Animals consume the carbohydrates and converted them back to carbon dioxide and water, in the process releasing and using the stored energy of the sunlight.

Carbohydrates are usually defined as polyhydroxy aldehydes (*e.g.* glucose) and ketones (*e.g.* fructose) or substances that hydrolyze to yield polyhydroxy aldehydes and ketones.

Carbohydrates containing an aldehyde group are collectively called '**aldoses**', while the ketonic sugars are referred to as '**ketoses**'. Thus, glucose is referred to as an **aldohexose** while fructose is an example of **ketohexose** (both glucose and fructose contain six carbon atoms and individual sugars end in the suffix -'ose', hence the name hexose). We shall later find that because carbohydrates contain >C=O and —OH groups, they exist, primarily, as **hemiacetals** and **acetals** or as **hemiketals** and **ketals**

The simplest hydrolysed products of carbohydrates are called **monosaccharides**. They cannot be further hydrolyzed into simple carbohydrates. On a molecular basis, carbohydrates that yield on

hydrolysis only two molecules of a monosaccharide are called **disaccharides** (*e.g.*, maltose and sucrose); those that yield three molecules of a monosaccharide are termed **trisaccharides**; and so on. At times, all such carbohydrates that produce 2 to 10 molecules of a monosaccharide on hydrolysis are called **oligosaccharides.** Carbohydrates that yield a large number of molecules of a monosaccharides (more than 10) are called **polysaccharides** *e.g.*, starch, glycogen and cellulose.

16.2.1. Monosaccharides

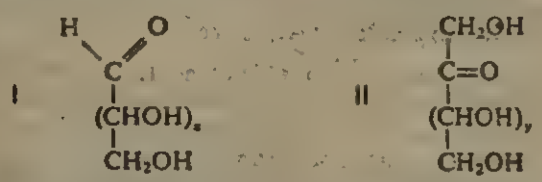
These are the simplest sugars which do not hydrolyze. There are about twenty monosaccharides which occur naturally. They are classified according to the number of carbon atoms present in the molecules as trioses, tetroses, pentoses, hexoses, and so on (Table 16·1). They have the general formula $(CH_2O)_n$.

TABLE 16.1. Monosaccharides

Class	*Molecular formula*	*Example*
Trioses	$C_3H_6O_3$	Glycerose
Tetroses	$C_4H_8O_4$	Erythrose
Pentoses	$C_5H_{10}O_5$	Ribose
Hexoses	$C_6H_{12}O_6$	Glucose, Fructose

The trioses are obtained as one of the products during the course of metabolic breakdown of the hexoses. Ribose, glucose and fructose are the important monosaccharides. The ribose (C_5 sugar) is an important chemical component of the nucleic acids.

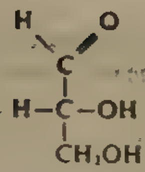
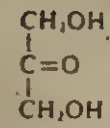
All monosaccharides may be represented by one of the structural formulae given below :



Aldoses ($x=1, 2, 3, 4, 5, ...$)

Ketoses ($y=0, 1, 2, 3, 4, 5, ...$)

The simplest monosaccharides are glyceraldehyde and dihydroxyacetone.

III  IV 

Glyceraldehyde (Aldotriose, $x=1$) | Dihydroxyacetone (Ketotriose, $y=0$)

Characteristics of monosaccharides

(*i*) Monosaccharides have asymmetric carbon atoms (chiral carbons) and, therefore, exhibit optical activity.

(*ii*) They are highly water soluble and get charred on heating and have sweet taste.

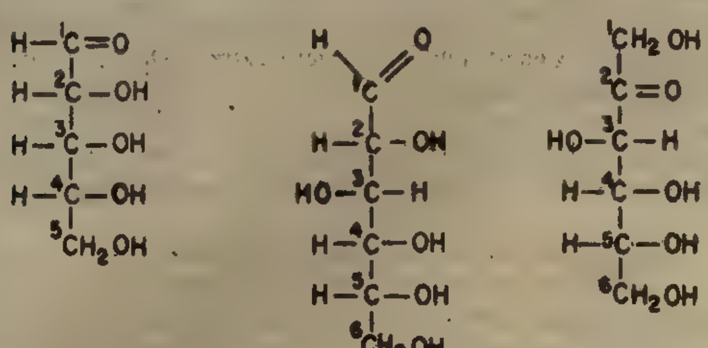
(*iii*) The free —OH groups can be completely acetylated and methylated.

(*iv*) Monosaccharides can be reduced to sugar alcohols.

(*v*) They can be oxidized at the aldehydic carbon to give acids (aldonic acids) and at the last primary —OH group to give uronic acids. When both the —CHO and —OH groups (primary) are oxidized, saccharic acid is produced

(*vi*) Two monosaccharides (same or different) on condensation give a disaccharide molecule.

The common open chain structures of the most common carbohydrates are portrayed below (Fig 16.1).



(I) Ribose (An aldopentose) | (II) Glucose (An aldohexose) | (III) Fructose (An ketohexose)

Fig. 16.1. Fischer projection formulae of monosaccharides.

The carbon atoms of an aldose are numbered from the aldehyde group and that of a ketose from the end closest to the ketone group.

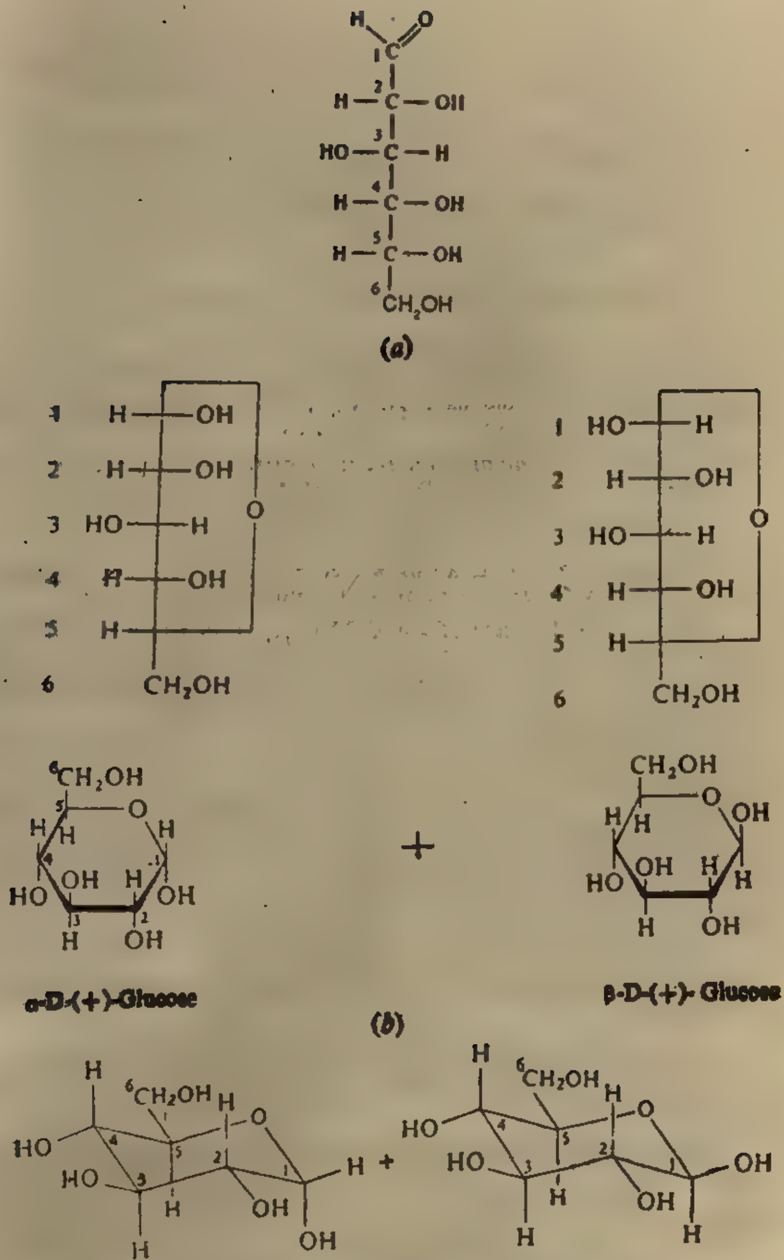
Glucose

A number of points emerge from the open chain structures. Firstly, there is a large number of hydroxyl groups. These, it is thought, are responsible for the sweet taste of sugars and are certainly responsible for their high solublility in water. In glucose, the hydroxyl groups at position 2, 3, 4, 5 and 6 are, in fact, typical alcoholic groups ; 6, being a primary alcohol group and the others secondary. Another point which emerges is that there are four asymmetric carbon (a carbon atom attached to four different atoms or groups is called asymmetric carbon atom and is said to possess a chiral centre) atoms in glucose (II), atoms 2, 3, 4 and 5 with a possibility of 16 isomers (8 DL pairs). The projection of the —OH groups was correctly deduced by Emil Fischer. Out of sixteen possible aldohexose isomers, only D-glucose, D-mannose and D- and L-galactose have been isolated from natural sources, while the others have been synthesized.

Symbols D- and L-relate to configurations in that they are not necessarily related to the optical rotations of the sugars to which they are applied. When hydroxyl group attached to the last asymmetric carbon (highest numbered sterocentre) which is farthest from the carbonyl carbon atom is on the right, the configuration is D- and if hydroxyl group is on the left the configuration is L-. On the basis of optical rotations, thus, one may encounter other sugars that are D-(+)- or D-(—)- and that are L-(+)- or L-(—)-.

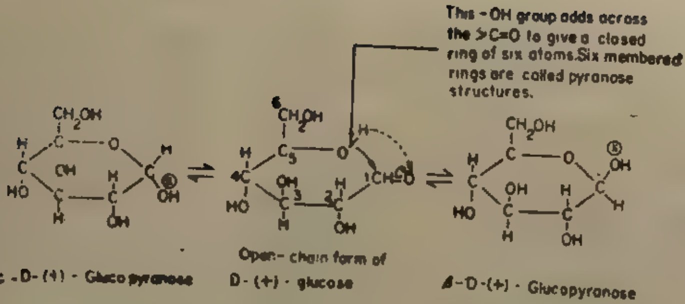
Although many of the properties of D-glucose (D(+) glucose) can be explained in terms of an open-chain structure (Fig 16·1 II), enough informations are available to suggest that the open-chain structure exists, primarily, in equilibrium with two cyclic forms (Fig 16.2).

The cyclic forms (Fig. 16.2) of D-(+)-glucose are **hemiacetals** formed by an intramolecular reaction of the —OH group at C-5 with the aldehyde group (Fig 16.3). The cyclization produces



(c) Chair forms (on the basis of X-ray studies)

Fig. 16.2. Open-chain structure of D-(+)-glucose, (b) and (c) Cyclic hemi-actals forms of D-(+)- glucose



(Starred —OH is the hemi-acetal --OH; this —OH group in α-glucose is on the opposite side of the ring from the —CH_2OH group at C-5; this —OH group in β-glucose is on the same side of the ring as the —CH_2OH group at C-5).

Fig. 16.3. The intramolecular reaction of the —OH group at C-5 with the aldehyde groups. This type of cyclization results in two structure of α-and β-glucoses (cyclic hemiacetal forms).

a new asymmetric carbon atom (stereocentre) at C-1 giving rise to in two diastereoisomers (or anomers) α-glucose and β-glucose.

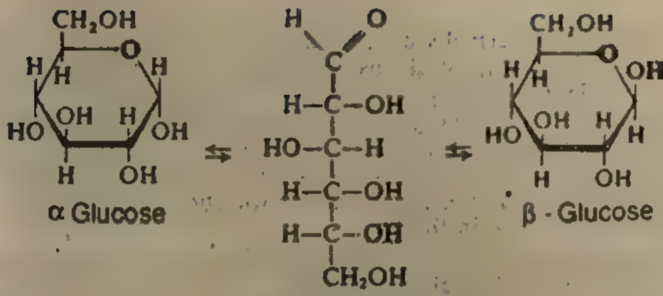
Structural difference of α and β forms is of high significance Starch, a polymer of α-glucose units is digestible. However, the enzyme systems of man distinguish and reject cellulose, polymer of β-glucose units, consequently, cellulose is indigestible.

The examination of α and β forms of glucose indicates that they are geometrical isomers. In α-glucose, the —CH_2OH group is trans to the —OH group at C-1. In β-glucose, the —CH_2OH group is cis to the —OH group at (C-1). Such isomers of a monosaccharide are called its **anomers**. The two forms (α and β) of glucose are found to exist in crystalline forms. They have different melting points and optical notations When either of the two is dissolved in water and the aqueous solution is allowed to stand, its optical rotation changes and attains an equilibrium value. This change is termed **mutarotation**. At equilibrium all the three forms of glucose exist.

Specific rotation of α-D-glucose is +112° and β-D-glucose is 18·7° but the mixture of these two forms acquires a constant value +52·7° with time.

When a small amount of gaseous hydrogen chloride is passed into a solution of D-(+) glucose in methanol, methyl acetals (both α and β forms) are formed (Fig 16·4). Carbohydrate acetals are called **glycosides** and an acetal of glucose is called a **glucoside**.

Glucose is the most abundant naturally occurring monosaccharide. It occurs in plants and animals. It is found in honey, ripe grapes, and other sweet fruits and in the blood and urine of

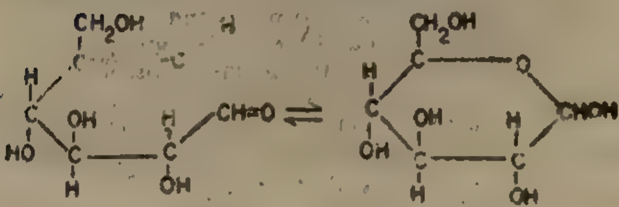


α Glucose

Open chain aldehyde form

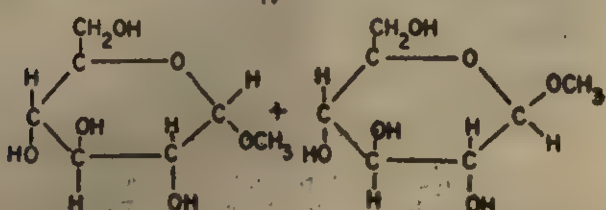
β - Glucose

α-D-(+) glucose (m p 146°, +112°) (36% at equilibrium)	⇌	D-glucose open claim (+52 7°) (0.024% at equilibrium)	⇌	β-D-(+)-glucose (m p 150°C, +18·7) (64% at equilibrium)



D (+) - Glucose Hemiacetal

HCl ⇅ CH_3OH



Methyl - α - D- glucopyranoside (mp 165°C) Methyl - β - D-glucopyranoside (mp 107°C)

Fig. 16·4. Formation of anomeric methyl acetals

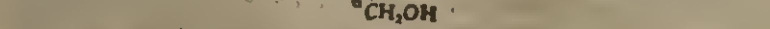
man. It is also found in saps of plants, blood, and tissue of cnimals. Depending on the source, it has been called grape sugar aorn sugar and blood sugar. It is also called dextrose.

Human body normally contains about 0.1 per cent of this sugar. Sometimes a solution of glucose is injected directly into the blood stream of patients seriously in need of nourishment, as it is the immediate source of energy for energy requiring cellular reactions in the body such as tissue repair, macromolecular synthesis, muscle movements, *etc.* An average adult has five to six grams of glucose in his blood. This can supply energy for about 15 minutes and is continuously replaced in the body.

Diabetic patient's body cannot assimilate glucose and this sugar is eliminated through the kidneys. The urine may contain as much as 8 to 10 per cent of glucose in such cases, and its presence there is one symptom of the disease.

Glucose is the major structural component of some important higher saccharides such as sucrose, maltose and lactose.

Fructose, a ketohexose, is commonly encountered in biochemistry. It is the sweetest of all monosaccharides. It occurs naturally with glucose in honey and ripe fruits. It exists in a number of cyclic forms, but in nature it is generally found as a five membered ring (furanose). Similar to glucose it also forms α and β form of fructose by an intramolecular reaction of the —OH group at C-5 with the ketonic group. When either of the forms is dissolved in water, the three forms (including the open form) exist in dynamic equilibrium (Fig 16·5). Fructose is also found in six membered ring form (pyranose), the actual conformations of the rings beings chair type.



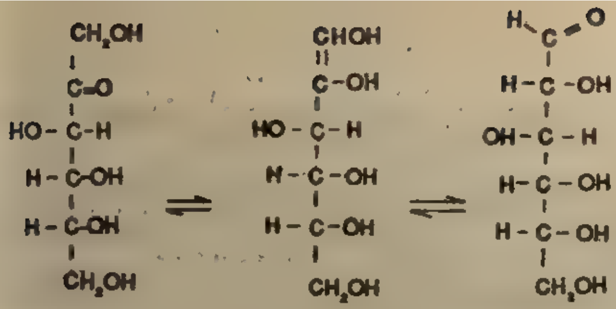
α-Fructose Open chain ketone form β-Fructose

Fig. 16.5. Fructose : Various forms that exist in aqueous solution are in dynamic equilibrium.

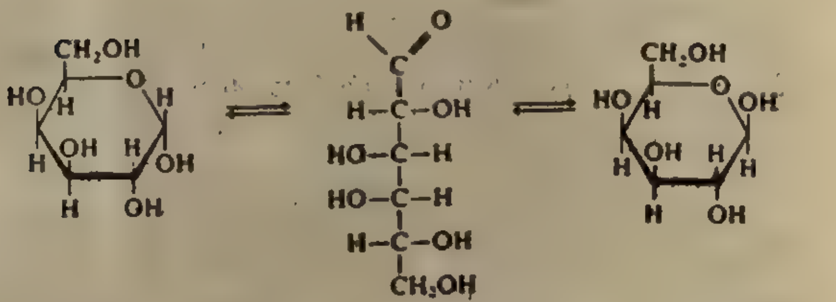
The ketonic group present in fructose does not confirm its reducing nature but its reactions with Fehling's and Benedict's solutions show its reducing nature. This is because of the fact that under alkaline conditions (both Fehling's and Benedict's solutions are alkaline reagents) all of the reducing sugars are slowly transformed into a mixtures of a number of $C_6H_{12}O_6$ isomers.

Thus alkaline reagents like Fehling's and Benedict's solutions do not differentiate between aldoses and ketoses.

Fructose is the sweetest of all the monosaccharides. It is the basic unit of insulin, a polysaccharide, thus it is the hydrolysis



Fructose Glucose



α Galactose open chain aldehyde form β - Galactose

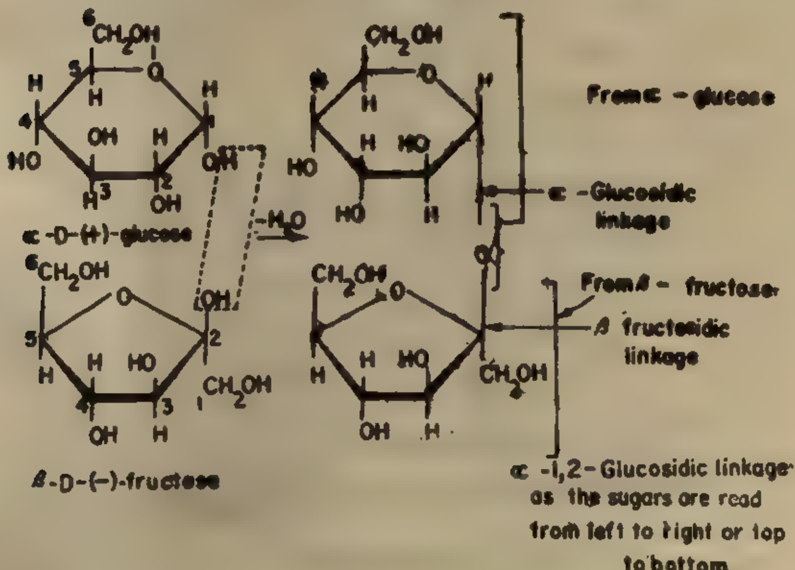


Fig. 16.6. Formation of sucrose, α-1, 2 glucoside linkage results from —OH group at C-1 of α-glucose and the —OH group at C-2 of β-fructose

product of insulin. It can be converted to glucose and in the liver and intestine, and hence, used in the body.

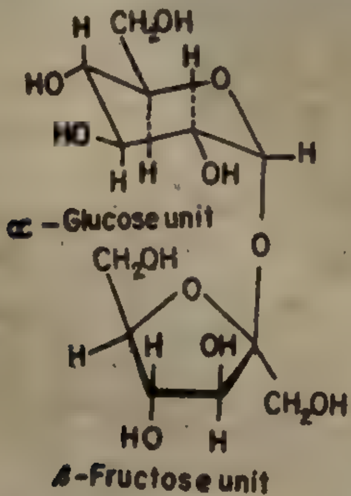
Galactose : It is not found directly in nature. It is obtained as one of the hydrolysis products of lactose, a disaccharide. It is a useful nutrient. It is also an aldohexose wherein the orientation of one of the hydroxyl groups is different from glucose. α-Galactose when dissolved into water is converted into an open chain form and into β-galactose.

16 2.2. Disaccharides

Disaccharides (general formula $C_{12}H_{22}O_{11}$) are sugars that consist of two monosaccharide units (the two units need not be the same) linked by an oxygen bridge. This forms an acetal (double ether) linkage called a **glycoside bond.** They can be hydrolyzed by enzyme action or by boiling with dilute mineral acids (also alkalis) to the constituent monosaccharides.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

We shall briefly discuss three important disaccharides: sucrose, lactose and maltose. Sucrose is ordinary table sugar. It is the most common sugar and is obtained commerially from sugarcane and sugar beets. It is a molecule of α-D-(+)-glucose which has been linked to one of β-D-(−) fructose by eliminating out a water molecule (Fig. 16 6). Sucrose can also be shown as given in Fig 16.7.



(α-D-glucopyranosyl β-D-fructo furanoside)

Sucrose, a disaccharide

Fig. 16.7. (a) Surcose, a disaccharide (α-D-glucopyranosyl-β-D-fructo furanoside)

Sucrose undergoes hydrolysis when catalyzed by acid or enzyme **sucrase** to form its daughter molecules glucose and fructose. The mixture of the two (1 : 1) is called **invert sugar** and is found n honey. It is not a reducing sugar as the —CHO and >C=O igroups are involved in glycosidic linkage. It is stable in aqueous solution.

Maltose (Fig. 16.8) or malt sugar contains two sugar units. It is formed by the action of an enzyme called **'diastase'** upon starch or by the partial hydrolysis of starch or dextrins by dilute acids. Maltose is fermentable in the presence of **yeast**, since yeast produces both **maltase**, which catalyzes the conversion of maltose to glucose and **zymase**, which catalyzes alcoholic fermentation of glucose. Lactose (Fig 16.9) occurs in the milk of cow to the extent of 5 per cent. It occurs to about 7% in human's milk. Pure lactose is obtained from whey the watery byproduct of cheese production. Hydrolysis in the presence of either dilute mineral acid or **lactase** converts lactose into glucose and galactose (an isomer of glucose). Certain microorganisms catalyze the fermentation of lactose to butyric acid or lactic acid. These acids are responsible for the souring of milk. Lactose is whole some food of infants.

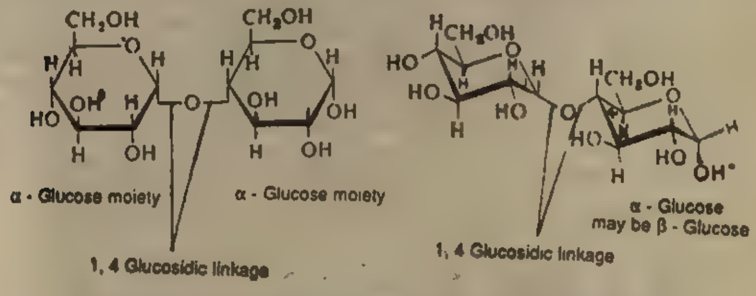


Fig. 16.8. Two representations of the molecule of maltoes [4-O (α-D-glucopyranosyl) α-D-gencopyranose]

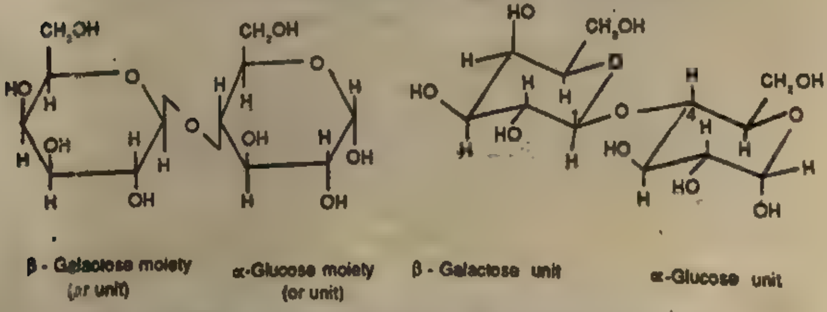
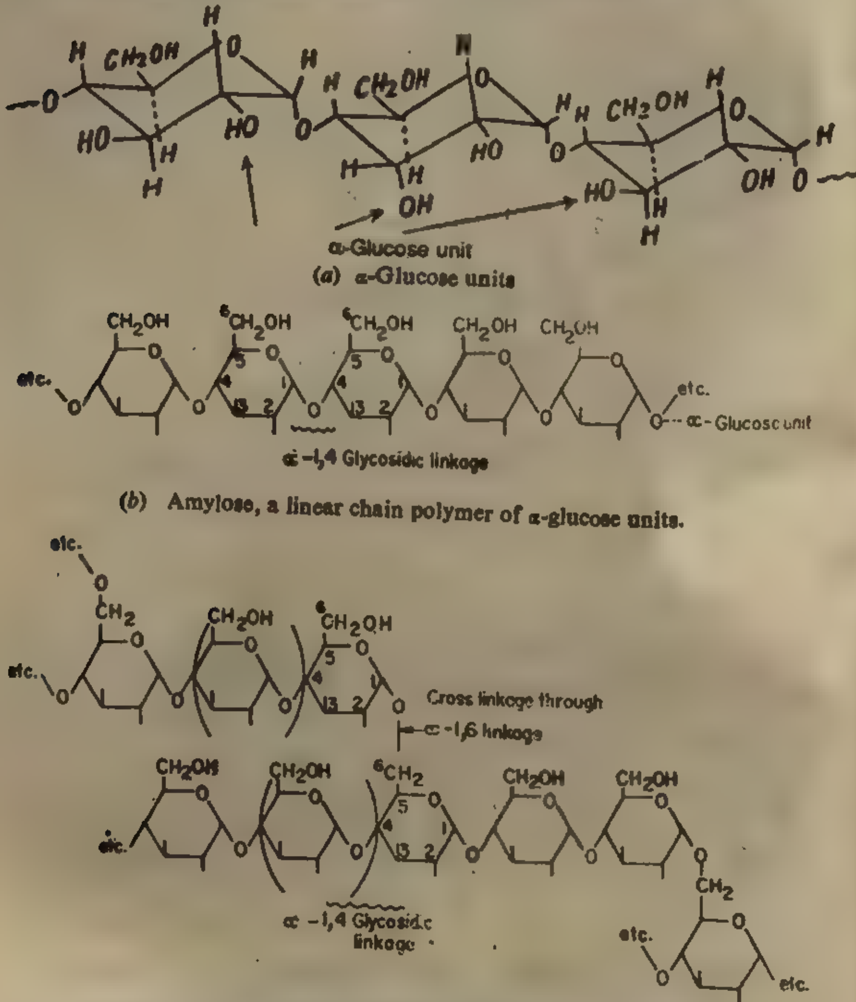


Fig. 16.9. Two representations of the molecule of lactose [4-O-(β-D-galactopyranosyl β-D-glucopyranose]

16.2.3. Polysaccharides

Three important polysaccharides, all of which are polymers of D-glucose, are starch, glycogen, and cellulose. The repeated condensation polymerization of monosaccharide units leads to the formation of a polysaccharide molecule. Individual sugar units may be connected to one another by glycoside linkage to form linear, branched, or circular polysaccharides. They are macromolecules (about 3,000 glucose units) of high molecular mass. They are hydrolyzed by mineral acids to monosaccharides



(a) α-Glucose units

(b) Amylose, a linear chain polymer of α-glucose units.

(c) Amylopectin, a highly branched polymer of α-glucose units

Fig. 16.10. Two components present in starch. The repeating unit is α-glucose.

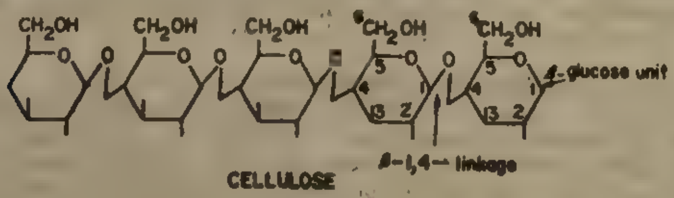
$$(C_6H_{10}O_5)\,n + n\,H_2O \longrightarrow n\,C_6H_{12}O_6$$

Their size place them in the colloids category. They are insoluble, but disperse in aqueous media as typical colloids. These do not possess reducing properties as potential aldehyde groups are destroyed by glycosidic linkages. Both homopolysaccharides (built of one type of monosaccharide) and heteropolysaccharides (built of two or more type of monosaccharides) are known.

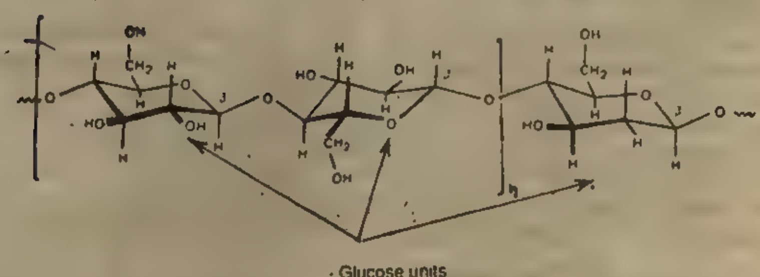
Starch is a polymer which is made of α-glucose units only. It is the major storage form of glucose in plants. It is accumulated by plants in roots, seeds, tubes and fruits. It is often the major food supply for the young plant until it has developed a leaf system and can manufacture its own food. It is an essential food source of carbohydrate and is found in cereals (wheat, rice or corn), potatoes legumes, and other vegetables. When starch is heated with water, its granules swell and produce a colloidal suspension which on anyalysis has been found to contain **amylose** (Fig. 16.10) and **amylopectin** (Fig. 16.10).

Amylose, the water soluble fraction, is linear in nature. Amylopectin is the water insoluble fraction and consists of branched chains of α-glucose.

The most abundant carbohydrate, indeed the most abundant organic compound is **cellulose**. It consists of β-glucose units joined by β-1,4glucosidic linkages to form long linear (unbranched) chains (Fig. 16·11). These chains pack together to



(*I*)



(*II*)

Fig. 16.11. Two representations of the arrangement of β-glucose units in cellulose, a linear polymer

form a strong rigid, insoluble and fibrous polymer. Such a material is ideal as cell-wall materials for plants. That is why cellulose serves as the main structural part of the cell-walls of all plants. Over 50 per cent of the total organic matter in the living world is cellulose. Wood is a combination of cellulose and lignin (it is also a polymer and a binding agent). Cotton is almost pure cellulose.

A typical chain length of cellulose contains from 3000—5000 β-glucose units repeatedly linked. The use of α-glucose in starch and that of β-glucose in cellulose is of high significance. It affects the chemical structure and properties of starch and cellulose. Cellulose is a linear polymer and mechanically much stronger than starch which is a branched polymer. It is interesting to note that an enzyme hydrolyzes either α or β linkage, but not both. Human beings can convert starch to its fuel form, glucose, but they lack enzymes to catalyze the hydrolysis of cellulose to glucose. Animals such as cows, sheep, goats and deer have intestinal bacteria that produce enzymes for breaking down cellulose into glucose. These animals can, therefore, use cellulose as a nutritional source.

Cellulose is a white amorphous solid, soluble in ammonical solution of $Cu(OH)_2$. It is also soluble in concentrated H_2SO_4. It can be nitrated to form cellulose nitrate which is used as an explosive. Intensive nitration produces guncotton a highly explosive compound. Viscose (cellulose xanthate) and acetate rayons processed from cellulose are important man-made fibers. Cellulose finds use in the manufacture of paper, celluloid, *etc.*

Glycogen, often called animal starch, is the storage form of carboydrate in animals. It is stored mainly in the liver and muscle and can be mobilized by enzymatic hydrolysis to glucose units. It has a structure very much like that of amylopectin ; however the chains in glycosen are highly branched. Its molecular mass may exceed 5 million. Its size and structure suit its functions as reserve carbohydrate for animals.

As you know, gum and pectins are two important food components. Gums are polysaccharides containing more than one type of monosaccharide residues. These are excreted by trees and shrubs. Their important property is gelling; they are used for thickening and improvement of texture in food industry. Pectins are present in fruit skins and are extracted by boiling. Jelly preparations contain pectin dissolved in a fruit juice and the pectin causes jelly to set into a semi-solid. Both gums and pectins are used in drug preparations.

16.2.4. Sugar and Sweetness

Mono-and disaccharides are sweet to taste. Their degree of sweetness varies. Fructose is the sweetest sugar. Now sugar substitutes are available. They are called artificial sweetners. They

are extensively used by people suffering from diabetics and weight watchers.

Saccharin, an artificial sweetener, is 500 times as sweet as sucrose. Some proteins and peptides have also been found to be sweeter than sugars.

TABLE 16.2

Compound	*Nature*	*Relative sweetness*
Cane sugar (sucrose)	Carbohydrate	100
Fructose	,,	173
Galactose	,,	32
Glucose	,,	74
Lactose	,,	16
Maltose	,,	32
Saccharin	,,	50,000
Aspartame	Peptide	160,000
Monallelin	Protein	20,00,000

16.3. PROTEINS

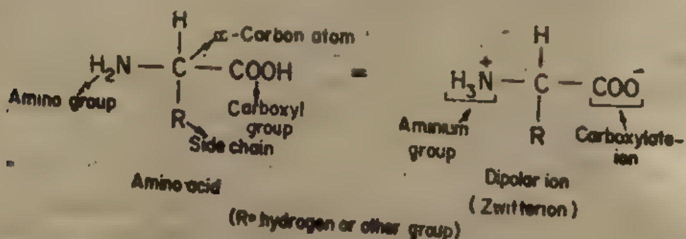
Of the three biopolymers—proteins, carbohydrates, nucleic acids—proteins perform the most diverse functions. As enzymes and hormones, they sustain life by catalyzing and regulating the reactions that occur in the body ; as muscles they supply power for movement, as skin and hair they give it a protective covering ; as haemoglobins they help in supplying oxygen to all parts of the body; as antibodies they fight against diseases and in combination with other substances in bone they give structural support to the body. Proteins are gigantic polymeric macromolecules of amino acids with high molecular mass produced in plants and animals. They are considered to be the building units of all vegetable and animal bodies. Proteins are essential part of the diet and are vital for the maintenance and growth of life. Thousands of different types of proteins go into the make up of a living cell. They take part in thousands of chemical reactions that occur in a living cell. The name protein is derived from the Greek word 'proteios' meaning first or primary, *i.e.*, compounds of primary importance. They contain the elements, carbon, hydrogen, nitrogen, oxygen and sometims sulphur and phosphorus. Proteins are built of long linear chains of some 20 different α-amino carboxylic acids Thus, proteins can be termed the polyamides from amino acids (monomeric units).

16.3.1 Amino Acids

Amino acids can be synthesized by all living organisms, plants and animals. All the twenty amino acids present in proteins are not synthesized by the animal's body and must be taken in as food. Such amino acids are called **essential amino acids**. Their number varies from one animal to another. Eight amino acids are essential for adult humans, *e g.*, lysine, methionine, threonine, tryptophan, phenylalanine, isoleucine, leucine and valine. Lack of essential amino acids in diet can cause diseases such as **Kwashiorkar.**

Animal proteins (meat, eggs, cheese and milk) contain most of the amino acids. The proteins in corn, rice and wheat have low lysine, tryptophan and threonine content. These are usually supplemented by protein-rich diets like pulses, *etc.*

Although there are structural differences among the common amino acids (Table 16·3), there are also certain similarities. They all contain an amino and a corboxyl groups attached to the same carbon atom and are designated α-amino acids. They all differ in the chemical nature of side chain, R. The general formula of an amino acid is given below :



Since amino acids contain both a basic group (—NH_2) and an acidic group (—COOH), they are amphoteric. In the dry solid state, they exist as **dipolar ions** (charged but electrically neutral). Such an ion is called zwitter ion (German two ions). In aqueous solution, an equilibrium exists between the dipolar ion and the anionic and cationic forms of an amino acid.

$$\underset{\substack{\text{Cationic form}\\\text{(present in strongly}\\\text{acidic solutions;}\\\text{pH 0 or so)}}}{H_3\overset{+}{N}-\underset{|}{\overset{}{C}}HCOOH}\ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}\ \underset{\substack{\text{Dipolar ion}\\\text{(H in neutral solution,}\\\text{pH 7·0 or so)}}}{H_3\overset{+}{N}-CH-COO^-}\ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}\ \underset{\substack{\text{Anionic form}\\\text{(present in strongly}\\\text{basic solution ;}\\\text{pH 14 or so)}}}{H_2NCHCOO^-}$$

(each form carries R on the α-carbon)

Further, α-carbon atom is asymmetrically substituted in all cases except glycine. Except glycine all amino acids are optically active. Among the naturally occurring some are dextro-rotatory while others are laevorotatory.

L-isomers of amino acids (Fig. 16.12) are exclusively present in proteins.

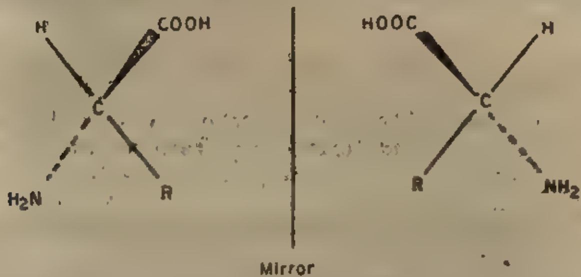
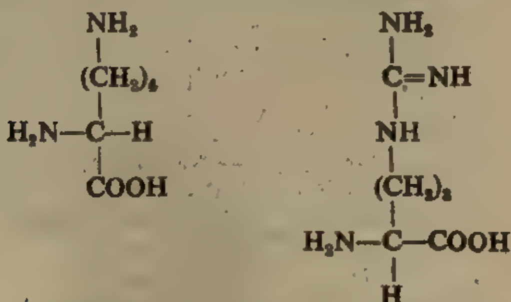


Fig. 16.12. Mirror images. Isomers of amino acids with stereocentre.

All synthesized amino acids are the racemic forms. In order to obtain the naturally occurring L-amino acid, the racemic form is resolved. Recently the ideal synthesis of L-amino acid by the use of chiral hydrogenation catalysts has been achieved. This type of synthetic reaction is called an **asymmetric synthesis** or **enantioselective synthesis.**

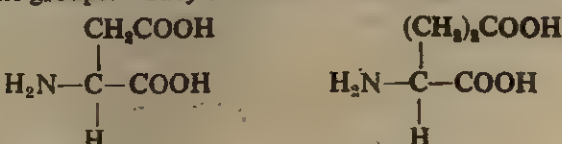
Amino acids like glycine and alanine ($CH_3CH(NH_2)COOH$ where $R=CH_3$) which contain one basic group and one acidic group are referred to as neutral acids.

Some amino acids have more than one basic group (other than the α-amino group) *e.g.*, lysine, arginine, etc.



Lysine   Arginine

Such amino acids are known as basic amino acids. Similarly some amino acids like aspartic acid and glutamic acid have additional acidic groups. They are called acidic amino acids.

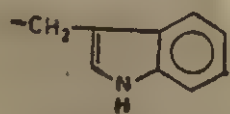
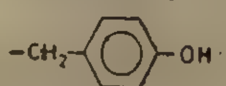


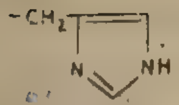
Aspartic acid   Glutamic acid

The amino acids differ with respect to the nature of their side chain groups —R. The difference in the properties of protein is due to nature of side chain (—R) in the amino acids which constitute the protein.

All amino acids have a basic group ($-NH_2$) and an acidic group ($-COOH$) which can react with each other or with other sources of acid or base. The most important reaction of amino acids is that which involve amide formation. Various amino acids are listed in Table 16.3.

TABLE 16.3. Structure of some naturally occurring amino acids

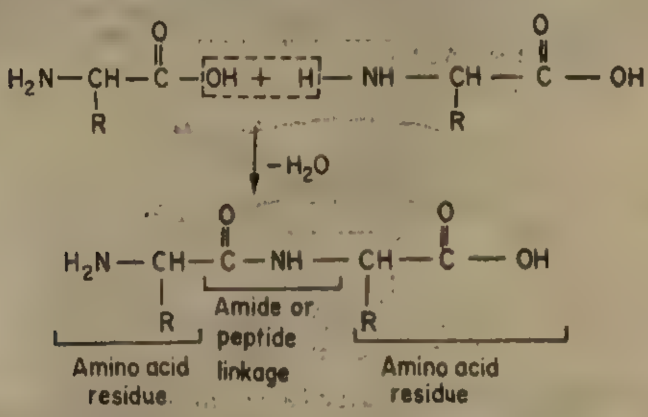
Amino acid	*Code or Symbol*	*Nature of side chain (—R)*
Non-polar (Hydrophobic)		
Alanine	**Ala**	$-CH_3$
Glycine	**Gly**	$-H$
Isoleucine*	**Ile**	$-CH(CH_3)-CH_2-CH_3$
Leucine*	**Leu**	$-CH_2-CH(CH_3)_2$
Methionine*	**Met**	$-CH_2-CH_2-S-CH_3$
Phenylalanine*	**Phe**	$-CH_2-C_6H_5$
Tryptophan*	**Trp**	
Valine*	**Val**	$-CH(CH_3)_2$
Polar (Neutral)		
Aspargine	**Asn**	$-CH_2-CONH_2$
Cysteine	**Cys (Cy)**	$-CH_2-SH$
Glutamine	**Gln**	$-CH_2-CH_2-CONH_2$
Serine	**Ser**	$-CH_2-OH$
Threonine*	**Thr**	$-CH(OH)-CH_3$
Tyrosine	**Tyr**	
Acidic		
Aspartic acid	**Asp**	$-CH_2-COOH$
Glutamic acid	**Glu**	$-CH_2-CH_2-COOH$
Basic		
Arginine	**Arg**	$-CH_2-(CH_2)_2-NH-C(=NH)-NH_2$

Histidine	His	
Lysine*	Lys	$—CH_2—(CH_2)_3—NH_2$
Proline	Pro	

*Essential amino acid.

16.3.2. Peptide Bond and Structure of Proteins

Amino acid units are linked together by condensation reaction involving the loss of a water molecule between each joined unit. The α-carboxyl group of one amino acid and the α-amino group of another join through amide linkage, —CO—NH— called peptide linkage. The resulting structures are called peptides. The indidual amino acid of a peptide is called amino acid residue.



Dipeptide

Depending on the number of amino acid residues per molecule, peptides are referred to as dipeptides, tripeptides and so on finally polypeptides. A protein molecule is a polypeptide and may contain hundreds or thousands of amino acid units joined in a linear fashion. Their molecular masses range from 15000 to 60000 or more. Each polypeptide can have any number of any one or the different types of amino acids which can be present in any sequence. Each polypeptide has one free carboxylic acid (- COOH) at one end which is called C-terminal and a free amino group at the other terminal which is called N-terminal

The polypeptide chain forms the backbone of primary structure of polypeptides and proteins, and may be represented as given in Fig. 16·13.

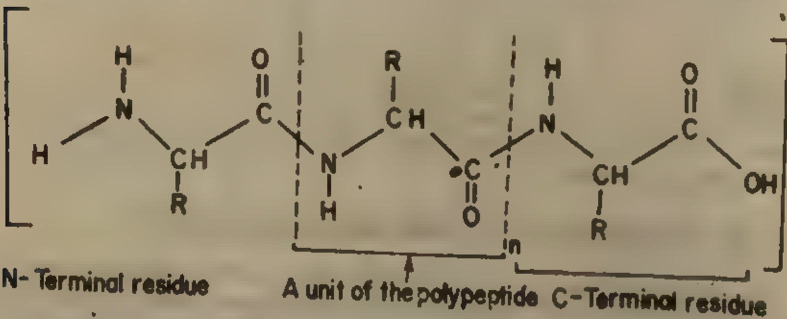


Fig. 16.13. Formula for primary polypeptide structure (R may be same or different)

The amide linkage (peptide linkage) is essentially planar since the nitrogen orbital containing a lone pair of electrons overlaps with the carbonyl electrons, and the electron density is spread over the O—C—N atoms (Fig. 16·14).

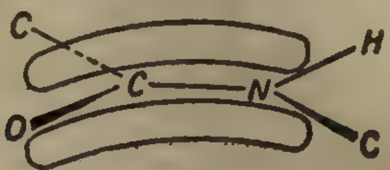


Fig. 16.14. Amide : Lone pair overlap with π electrons

This type of overlap imposes a barrier to rotation about the carbonyl C—N bond. Protein chains, however, can twist, curle or entwine because of the asymmetric carbon atom between the nitrogen atom and carbonyl carbon atom (Fig. 16.15). These discoveries have been made through the application of X-ray diffraction techniques ; much of the credit for this very important work goes to Linus Pauling who received the Nobel Award in 1954.

Primary Structure of Proteins

The basic chemical structure of proteins was determined by the German chemist Emil Fischer between 1900—1910. Through his studies he established the presence of peptide bonds. Protein molecules differ among one another not only in the number and

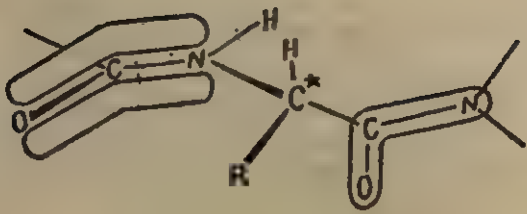


Fig. 16.15. Twisting of protein chain

kind of amino acid residues but also in the order in which the residues are arranged in the polypeptide chains. This means that the number of possible protein structures is very large. Each protein has a distinct order of arrangement of the amino acids in the peptide chain. This order of arrangement is called the primary structure of the protein. The amino acid sequence of a protein determines its function and is critical to its biological activity; when even one amino acid is substituted for another, the biological function may be totally altered. A classical example of this phenomenon occurs in the disease sickle-cell anemia. The haemoglobin polypeptide of normal people contains the following sequence of amino acids linkages :

Normal Haemoglobin—Val—His—Leu—Thr—Pro—*Glu*—Glu—Lys—

In patients suffering with sickle-cell anemia the sequence is :

Sickle cell haemoglobin—Val—His—Leu—Thr—Pro—*Val*—Glu—Lys—

The substitution of valine (Val) for glutamic (Glu) acid totally alters the function of normal haemoglobin *i.e.*, changed haemoglobin does not transport oxygen.

The determination of amino acid sequence in a protein is a complex procedure that was first developed in 1945 by Frederic Sanger. He established the primary structure of protein hormone insulim. For this work he was awarded a NOBEL PRIZE in 1958. The complete amino acid sequences present in several hundred proteins are now known.

Insulin has 51 amino acids arranged in two polypeptide chains which are cross-linked at two places by disulfide bonds (Fig. 16.16). One chain contains 21 amino acid units and the other has 30 amino acids, the total molecular mass being 5733.

Pancreas of cattle are the principal sources of insulin. Through genetic engineering, it has been possible to synthesize insulin. It regulates glucose metabolism. Insulin deficiency in humans is the major problem in diabetes mellitus.

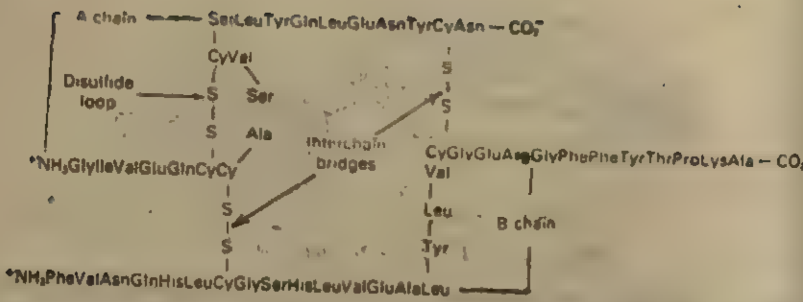


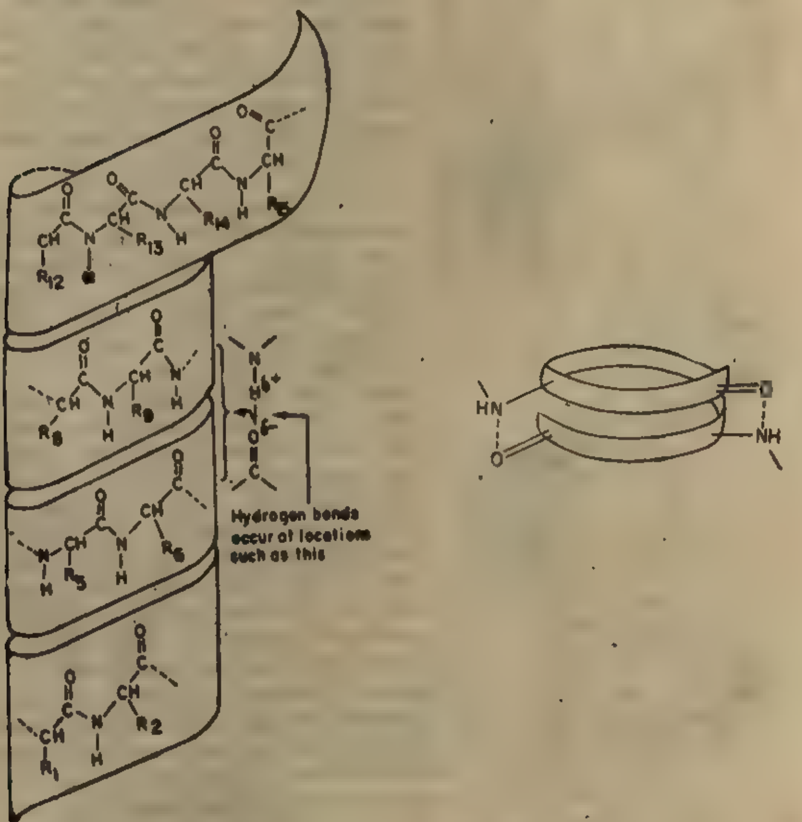
Fig. 16·16. The amino acid sequence of bovine insulin. Chain A and chain B are joined through S—S—cross linkages at two places. Chain A has an additional disulphide linkage at positions 6 and 11. Human insulin differs bovinine insulin. In human insulin, threonine replaces alanine (residue 8) in chain A and alanine (residue 30) in chain B ; isoleucine replaces valine (residue 10) in chain A.

Secondary Structure of Proteins

The secondary structure of a protein is the way in which the amino acid chain is folded or bent. Polypeptide chains are quite flexible and can take on many different shapes. Polypeptide chains tend to form random coils or to adopt helical or sheet structures. This has been possible because the flexible polypeptide chains could be stabilized by hydrogen bonds, extending from the hydrogen attached to the nitrogen of one amino acid residue group to the carbonyl oxygen of another amino acid residue. Two types of shapes that occur frequently in proteins are the **α-helix**, a spiral arrangement of the polypeptide chain (Fig. 16.17), because of intramolecular hydrogen bonding within a chain, and the **β-structure** (Fig. 16·18) intermolecular hydrogen bonding between two adjacent polypeptide chains), an arrangement of pleated or puckered sheet.

The α-structure is a right handed helix, a spiral turning in the direction of right hand screw. On an average there are 3.6 amino acid residues per turn of the coil. Each amino acid residue forms a hydrogen bond through its carbonyl oxygen with the N-H hydrogen of the fourth residue. Although hydrogen bonds are weak, the cumulative effect of several hundred hydrogen bonds in a protein molecule is enough to ensure structural integrity. This

type of integrity is imperative to the biological functions of the protein and if it is irreversibly destroyed the protein can no longer function. This α-helix structure is found in many proteins. Fibrous proteins such as myosin, the protein muscle



(a) Peptide chain tends to coil into a right handed α-helix.

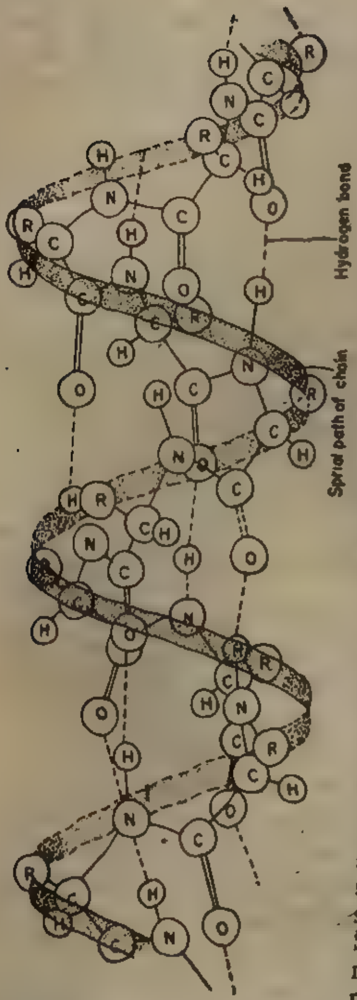


Fig. 16.17. Helical structure of protein. (a) Peptide chain tends to coil into a right handed α-helix. This coiling produces a three-dimensional tubular aspect to the peptide chain (b)Hydrogen bonds between H of one amino acid residue and carbonyl oxygen of another amino acid residue hold the chain in this position

And of α-keratin, the protein of hair (collagen), unstretched wool, and nails have α-helical structure. Such proteins tend to be long, rod shaped molecules with great mechanical strength. These proteins possess elastic nature. On stretching the molecules of proteins, the weak hydrogen bonds are broken, and thus, tend to increase in length like a spring. On releasing the tension, the hydrogen bonds are reformed, and thus, help the protein molecules to acquire their original shape.

The beta pleated sheet protein consists of peptide chain arranged side by side to form a structure that resembles a piece of paper folded into many pleats. The carbonyl groups of one peptide chain are hydrogen bonded to N-H hydrogens of adjacent peptide chain that run in opposite directions so that the N-terminal of one get oriented against the C-terminal of other. In fact, a number of such chains can be interbonded together to form a sheet. Such sheets tend to stack one upon another to form three dimensional structure called a beta pleated sheet. Such sheets are formed by separate strands of protein or by a single chain looping back on itself. Silk possesses structure of this nature with the protein chains running in the direction of silk fibres. This arrangement imparts to silk its characteristic mechanical properties. Silk fibre is not elastic. On stretching, the covalent linkages are destroyed. On the other hand, silk fibres can bend easily because its protein sheets can slide over each other. Silk fibroin is an example of fibrous proteins. The proteins present in stretched hair and muscle and wool have been

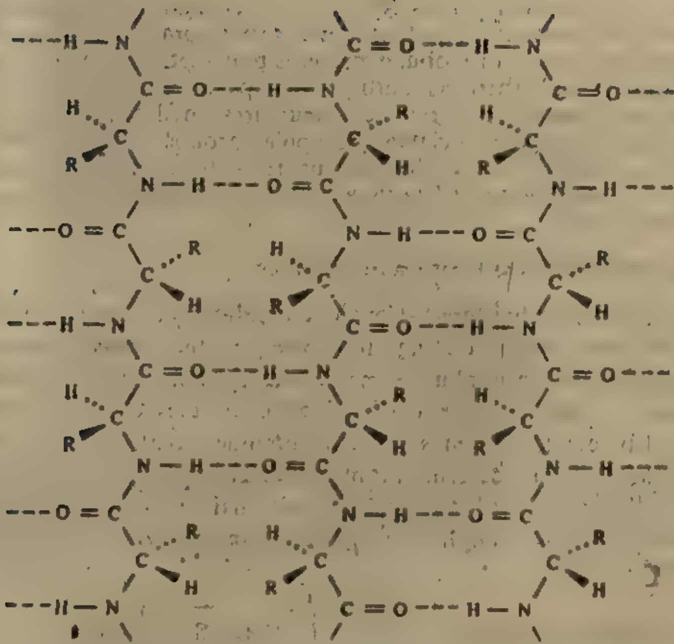


Fig. 16.18. Rrepresentation of the beta pleated sheet structure of polypeptides. The dashed lines show hydrogen bonds (R=H or CH_3)

shown by X-ray analysis to possess polypeptide chains arranged in parrallel fashion forming sheets.

Tertiary Structure

The tertiary structure of a protein is its three dimensional shape that arises from further foldings of its coiled polypeptide chains, foldings superimposed on the coils of α-helixes. The tertiary structure of a protein is controlled by several different kinds of interactions that serve to hold the folded segments of the chain in place. Such interactions depend upon the nature of side chains present in the amino acid.

At normal pH and temperature, each protein will take a shape that is energetically most stable This shape is specific to a given amino acid sequence and is called the native state of the protein. Proteins have been found to retain their helical structure even in aqueous solution.

Globular proteins possess tertiary structure. In general, these proteins are very tightly folded into a compact spherical form main-

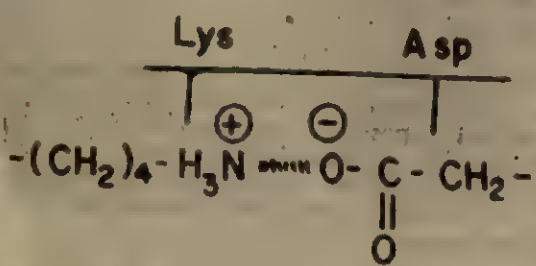
tained by certain interactions between the side chains. Such proteins are insoluble in water. Their structure is very complex as compared to fibrous proteins. In globular proteins polypeptides are very compactly folded, and there is hardly any space in the interior for traping water molecules. In such structures, hydrophobic groups point inward and get associated ; the polar groups being present on the surface which forces globular proteins to acquire spheroidal shape *e.g.*, myoglobin of skeletal muscle and haemoglobin present in red blood cell.

Forces that Stablize Protein Structures

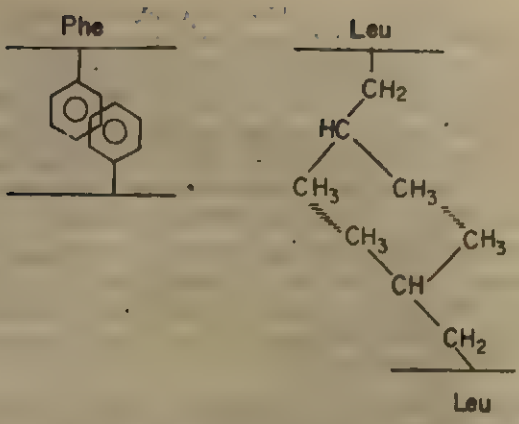
Disulphide bridges. Covalent bonding is the most common form of inter-chain bonding, for example, the disulphide bond formed between the sulphur atoms of two cysteine residues. Intermolecularly, specific segments of a single chain may be held together or coiled by disulphide links. The disulphide bonds are an important factor in the determination of the gross shape of a protein. The insulin consists of two polypeptide chains A and B which are linked together by disulphide bridges, and in addition, an interchain disulphide bond.

$$\{ CH_2{-}SH + SH{-}CH_2{-} \} \overset{[O]}{\rightleftharpoons} \{ {-}CH_2{-}\underbrace{S{-}S}_{\text{Disulphide bridge}}{-}CH_2 \}$$

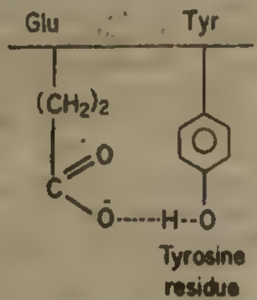
Ionic bonds (salt bridges). Acid-base interactions can take place between the side chains of basic residues of amino acids such as lysine and arginine an acidic residues such as aspartic and glutamic acids.



Hydrophobic (a polar) bonds. Amino acid residues of acids such as leucine and phenylalanine have hydrophobic (water hating) side chains. In aqueous solution, they tend to associate as non-polar entities, excluding themselves from the aqueous phase. Such an association in aqueous solution is termed hydrophobic bond. The side polar chains which behave as hydrophilic (water loving) groups lie on the outer surface of proteins.



Side chain hydrogen bonds. Both side chain and intrapeptide hydrogen bonds are possible. Certain polar groups present in certain amino acid residues, for example, phenolic tyrosine residue can hydrogen bond to carboxyl group.



Quarternary Structure

The secondary and tertiary structures are an outgrowth of the primary structure of a protein. Quarternary structures arise if several pylypeptide chains in some lateral fashion aggregate together as a unit (not being linked to one another by covalent bonds). They are held together by a variety of surface interactions including those between side chains of residues and exposed portions of the peptide backbone. Haemoglobin is a protein with quarternary structure, consisting of four subunits.

16.3.3. Shape and Biochemical Functions of Proteins

Proteins exist as rather tight, compact structures, which are highly and specifically folded. The gross shape of a protein is

related to its biological function. Proteins are among the most important types of substances present in living cells. The human body contains many thousands of different proteins each with a special structure that permits it to exhibit a specific function.

Protein is a good source of energy (necessary for various metabolic processes). They are the essential constituents and building blocks of various tissues. Various enzymes present in the cells are primarily proteins which act as biological catalysts.

Hormones of the body are also proteins. Hormone insulin which is secreted in pancreas is responsible for the maintenance of sugar level of the body. There are numerous structural proteins like collagen in tendon, keratin in skin, hair, silk, nails, horn and feathers, myosin in muscles.

Some blood proteins form antibodies, which provide resistance to disease, while the so-called nucleoproteins are important constituent of the genes that supply and transmit genetic information in cell division.

Proteins are helpful in transporting the cellular necessities such as oxygen, metals, fatty acids, hormones, *etc.* The haemeglobin molecule contain, the protein molecule globin which is responsible for the transport of oxygen throughout the body. Some of the proteins are simply present as food reserve. The ovalbumin of egg white and the casein af milk are such proteins. Ovalbumin degrades at the time of requirement for use by growing chick; casein similarly nourishes the new born mammal.

Proteins are essential constituents of foods. During digestion in the stomach by the action of pepsin, they are hydolyzed into amino acids. These amino acids pass through the walls of stomach and intestines into the blood stream the blood carries the amino acids to tissues, where they are converted into specific proteins required by the body under the influence of nucleic acids. Thus tissue proteins are in a state of dynamic equilibrium, undergoing constant degradation and resynthesis. Proteins act as a source of amino acid in a growing embryo, *e.g.*, gliadin (protein) of wheat seeds and ovalbumin of egg white. Blood proteins thrombin and fibrinogen are involved in blood clotting.

16.3.4. Denaturation of Proteins

A protein molecule whose peptide chains are folded in their normal, physiologically active way is in its native state. Denaturation occurs when the peptide chains of a native protein unfold. Protein molecules tend to unfold and lose their characteristic shapes when exposed to heat, extreme pH or non-aqueous solvents. These reactions called 'denaturations' change the physical properties of proteins and destroy their biological activity. Coagulation of egg

albumin (white of an egg) by heat is familiar example of **denaturation**. Concentrated acids, bases, strong electrolytes and heavy metal ions (Hg^+, Ag^+, *eta.*) also help in denaturation (Fig. 16·19).

Raw egg white, a globular protein, is a soluble form of protein. It gets converted into fibrous form and gets coagulated and becomes hard on boiling. Preparation of cheese is also a familiar example of protein denaturation.

When pH of milk is brought at 4·5 or below, casein (milk protein) precipitates and cheese is formed which is an insoluble form of milk protein.

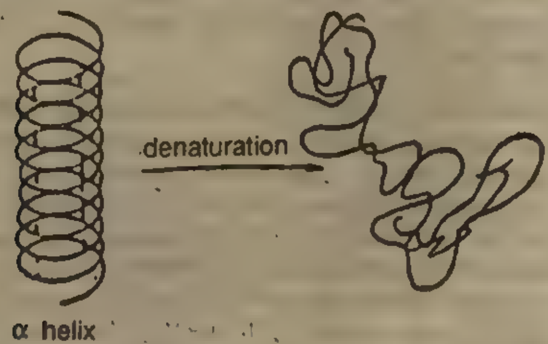


Fig. 16.19. Opening of folded structure during denaturation.

16.4. ENZYMES

Unlike many reactions in a laboratory, most of the biochemical reactions in cells take place in aqueous solutions (a cell contains about 70 per cent water) at pH 7.0, at physiological temperatures (37°C or 310 K) and at atmospheric pressure. Under these conditions, these reactions are not likely to take place at a significant rate without taking the help of catalysts Such catalysts which speed up biochemical reactions are called enzymes. Therefore enzymes are biological catalysts. Enzymes also provide the organism with a way of controlling the rates of the reactions that take place. In fact, enzymes direct the chemical reactions that take place in a living cell, and also catalyse a reaction of the cell.

Enzymes are globular proteins. They constitute a major portion of the total protein of the cell. A typical cell contains about 3000 different kinds of enzymes. They are produced by a living cell aud also catalyse the reactions of the cell.

This ability of producing enzymes is passed from one generation to another generation.

Enzymes have the following characteristics :

—Remain unchanged during the course of reaction.

—Do not change the normal position of chemical equilibrium.

—Act as a catalyst for a specific chemical reaction-specificity.

—Act efficiently - the rate of some reactions is increased several hundred thousand fold (10[illegible]) in the presence of an enzyme.

As regards the state of chemical equilibrium, reactions in cells ever reach equilibrium because the products are rapidly converted to another substance in another enzyme-catalyzed reaction.

Enzymes are highly specific in their action on substrates (the molecule on which they act) and each enzyme catalyzes only a specific type of reaction.

They catalyse a reaction involving a specific substrate only but do not catalyse reactions involving closely related substrates. They are often named according to the substrate they affect. For example, the enzyme maltase catalyzes the hydrolysis of maltose but has no effect upon the hydrolysis of 'sucrose or lactose. Similarly, sucrase catalyzes the hydrolysis of sucrose, but not maltose or lactose. Lactase catalyzes the hydrolysis of lactose, not maltose or sucrose. None of these enzyme will speed up the rate of hydrolysis of proteins, fats, etc.

The catalytic power of an enzyme is exceedingly higher than a non-biological catalyst. One molecule of enzyme can bring about the decomposition of many millions of substrate molecules per minute. Thus even small amounts of enzymes show high catalytic efficiency. The enzyme molecules are regenerated during their catalytic activity (just as the chemical catalysts). A typical enzyme may be regenerated a million times in one minute.

Many enzymes require some non-protein components for their effective functioning. These components could be metal ions and smaller organic molecules called coenzymes. Some of the metal ions involved are, Co^{2+} Zn^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, K^{+} and Na^{+}. Many vitamins that you normally consume to maintain good health are precursors of coenzymes. Many of the coenzymes are derived from vitamins of B-group. Vitamin B_{12}, whose deficiency in the diet causes a disease known as pernicious anemia, is changed into its coenzyme in the body. Some examples of enzymes and their functions are given in Table 16·4.

TABLE 16.4. Enzymes and the reaction which they catalyze

Enzyme	*Substrate*	*Product*	*Nature of catalyzed reaction*
1. Amylase	Starch	Glucose	Hynrolysis
2. Carbonic anhydrase	H_2CO_3	CO_2 and H_2O	Decomposition
3. Invertase	Sucrose	Glucose and fructose	Hydrolysis
4. Lactase	Lactose	Glucose and galactose	Hydrolysis
5. Maltase	Maltose	Glucose	Hydrolysis
6. Pepsin	Proteins	Amino acids	Hydrolysis
7. Urease	Urea	CO_2 and NH_3	Decomposition
8. Trypsin	Proteins	Amino acids	Hydrolysis
9. Nucleases	DNA, RNA	Nucleotides	Hydrolysis
10. DNA polymerase	Deoxynucleotide triphosphates	DNA	Polymerization
11. RNA polymerase	Ribonucleotide triphosphate	RNA	Polymerization

Mechanism of Enzyme Action

The catalytic activity of an enzyme seems to be the greatest of all catalysts. The mode of its action is the same as that of any other catalyst, *i.e.*, it increases the rate of reaction by lowering the energy of activation for the reaction or process.

The plausible mechanism of enzyme action involves a reactant species called the substrate (S). It attacks the active site on the enzyme (E) and forms a complex (ES). In due course the complex decomposes to produce a product species (P) and the original enzyme (E). Thus, a two step mechanism is,

$$S+E \longrightarrow ES$$
$$ES \longrightarrow E+P$$

The binding site is apparently so specific and shaped that it can bind only one or only one kind of substrate molecule (Fig. 16·20). The specificity has been compared to a lock and key.

In all such enzymatic reactions the first step is reversible followed by an irreversible step. The reaction rate increases with the concentration of substrate until a stage is reached when further

addition of substrate does not affect the rate. Enzyme's activity is also affected by temperature and pH.

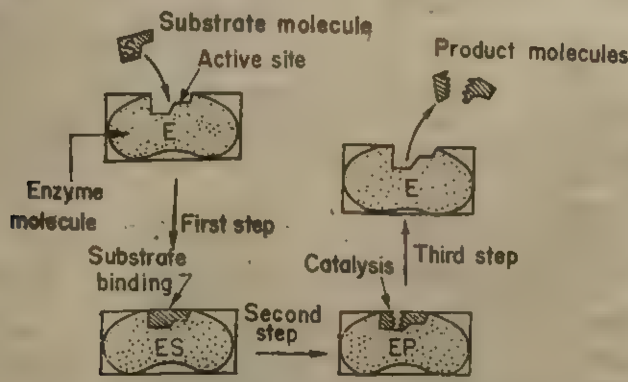


Fig. 16.20. Interaction of a substrate molecule with an enzyme molecule. The active site on the enzyme and the active site on the substrate are complementary and thereby fit together

In view of their efficiency and specificity, enzymes are widely used in industries, Almost all fermentation processes, *e.g.*, manufacture of beer, wines and spirits, *etc.*, involve the use of enzymes. They are used in bread making and used as additives in food stuffs, washing powders and pharmaceutical products.

Enzymes and Diseases

A human body with a genetic defect (absence of an enzyme) does not function effectively. In some case, an enzyme deficiency is caused by the dietary deficiency. For example, vitamins are needed to synthesize certain enzymes. Long absence of a particular vitamin in our food can cause disease and even death. Thus the symptoms of the vitamin deficiency may be correlated to the deficiency of certain enzymes. The congenital disease **phenylketone urea,** is caused by the deficiency of the enzyme **phenylalanine hydroxylase.** As a result of disease, certain compounds accumulate in the body which lead to brain damage and mental retardation in children. This disease can be prevented by consuming food with a low phenylalanine content. Albinism is another disease which is related to the deficiency of an enzyme tyrosinase. Some enzymes find use in treating heart diseases. Many heart attacks are caused by clotting of blood in a coronary artery. These days an enzyme **streptokinase** is being used to dissolve the clot.

16.5. NUCLEIC ACIDS

There are several organelles immersed in cellular fluid or

cytoplasm. The nucleus and mitochondria (Unit 19, class XI) are the two important organelles wherein many biochemical reactions take place. Certain chemical substances called **nucleic acids** also occur in the cytoplasm and protoplasm (dense mass making the nucleus is called protoplasm).

No area of scientific enquiry in the 20th century has generated more interest and speculation than the study of nucleic acids.

One of the most mysterious aspects of life is the ability of living organisms to reproduce themselves. The fact that organisms are involved in reproducing their own species, continue to keep busy the chemists world over. **This reproduction is the self duplication of a cell by division**. For a cell to live for ever, it is necessary that it must have a record of amino acid sequences, enzymes and proteins as they are the raw materials for the poduction of new cells and to repair damaged cells. From different proteins different types of species will emerge. Thus, when a cell gets subdivided into two new cells, it is desired that they are equipped with identical information about their proteins.

How is this genetic information stored and transmitted within an organism (cell), and between parent and offspring ? This basic question of life and the mechanism of heredity has been the most challenging problems facing science today. This problem has been partly solved by the determination of the molecular structure of nucleic acids. Nucleic acids are the important constituents of the nuclei of all living cells.

Johannes Miescher discovered nucleic acids from pus cells in 1869. Nucleic acids are macromolecules with high molecular masses. The nucleic acid macromolecules are of two major types : deoxyribose nucleic acids (DNA) and ribose nucleic acids (RNA). DNA is found in the nucleus of the cell while RNA is found in the cellular fluid outside the nucleus, the cytoplasm. Both being acidic are found bonded to proteins and the complexes are called nucleoproteins. They are, however, chemically quite distinct from proteins and are made up from nucleic acid units. Both are essential for the biosynthesis of proteins.

Within the nucleus there are giant nucleoprotein molecules that biologists oall chromosomes. DNA constitutes parts of the chromosomes. Specific sequences of arrangement of the DNA groups on the chromosome are called **genes**. Genes determine all aspects of your body, structure and functions. They exercise their superiority at least in part by determining what enzymes your cells can produce. Chromosomes and genes occur in pairs. You inherited one gene of each pair from one parent and one from the other parent.

Nucleic acids make up less than one per cent of the organic compounds present in the cells of living organisms ; yet these compounds are imperative to life. They control all the chemical reactions of the cell and are responsible for the reproduction and transmission of hereditary information. Thus, nucleic acids carry genetic information as a chemical code that is passed on from one cell to another as they divide, and from one generation to another as organisms reproduce.

16.5.1. Nucleotides and Nucleosides

Nucleic acids are polymers of simple units called nucleotides (monomeric units). The partial hydrolysis of nucleoprotein yields nucleotides and nucleosides which, in turn, on hydrolysis give certain bases, pentoses and phosphates. The complete hydrolysis of nucleoprotein is outlined below :

$$\text{Nucleoprotein} \xrightarrow{H^+} \underset{\text{(base+pentose+phosphate)}}{\text{Nucleotide}} + \text{protein}$$

$$\downarrow H^+$$

$$\underset{\text{(base+pentose)}}{\text{Nucleoside}} + \text{phosphate}$$

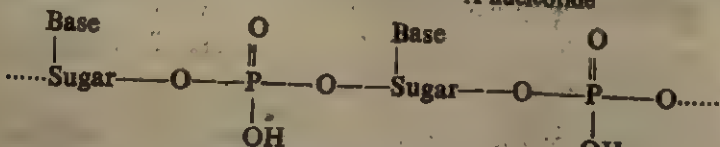
$$\downarrow H^+$$

$$\text{Purine or pyrimidine} + \text{pentose (sugar)}$$

A typical nucleic acid would have hundreds of nucleotides joined via esterification of the sugar moiety with phosphate, *i.e.*,

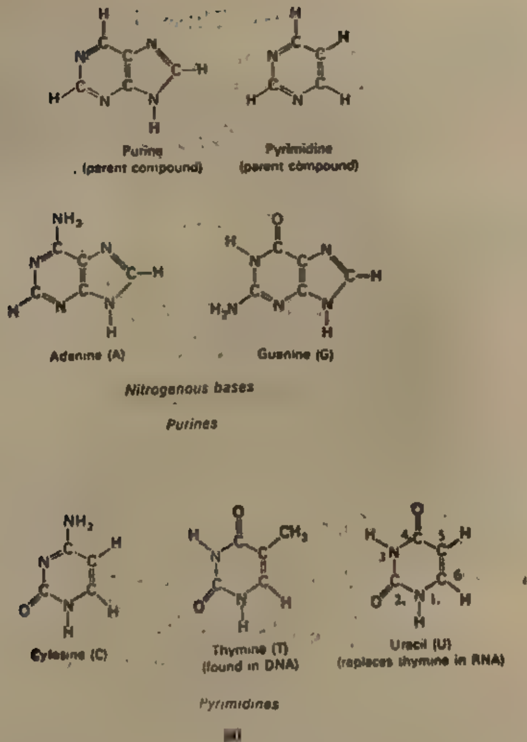
$$\boxed{\text{Base}} + \boxed{\text{Sugar}} \longrightarrow \underbrace{\boxed{\text{Base}} - \boxed{\text{Sugar}}}_{\text{A nucleoside}}$$

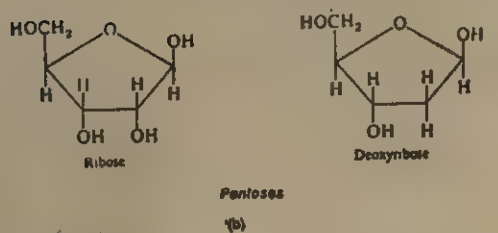
$$\underbrace{\boxed{\text{Base}} - \boxed{\text{Sugar}}}_{\text{A nucleoside}} + \boxed{\text{Phosphate}} \rightarrow \underbrace{\boxed{\text{Base}} - \boxed{\text{Sugar}} - \boxed{\text{Posphate}}}_{\text{A nucleotide}}$$



Polynucleotide chain
(Base=Purine or pyrimidine)

Now it can be inferred that the units of nucleic acids, *i.e.*, nucleosides consist of three components (Fig. 16.21).





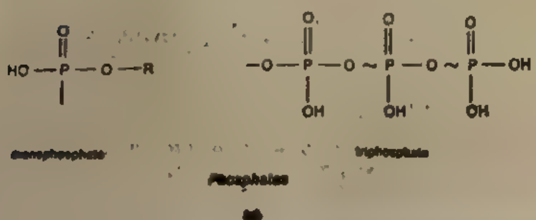


Fig. 16.21. The vital components of a nucleotide (a) bases, (b) sugars, and (c) phosphate groups

(*i*) Two classes of heterocyclic ring compounds containing nitrogen, purines and pyrimidines. These are called bases.

The bases derived from purine are adenine (A) and guanine (G). Those derived from pyrimidine are cytosine (C), thymine (T) and uracil (U). The base uracil is found only in nucleotides of RNA and the base thymine is found only in nucleotides of DNA.

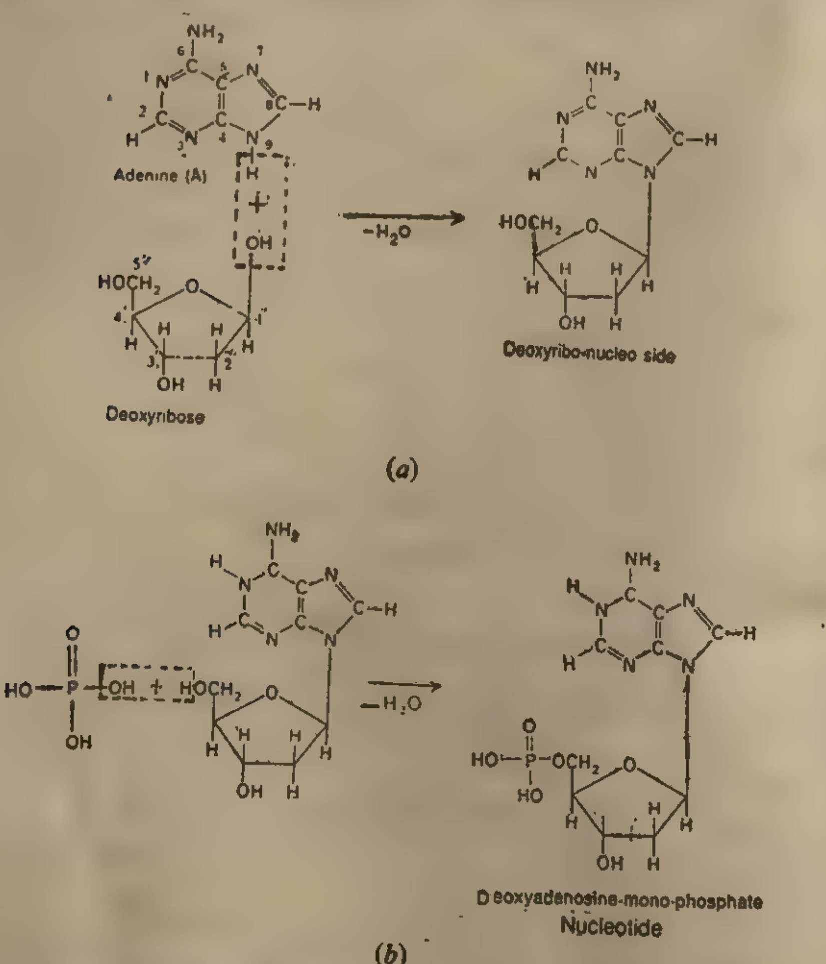


Fig. 16.22. The formation of typical nucleoside and nucleotide
(*a*) *a purine or pyrimidine*
$+$ → *a nucleoside*
ribose or deoxyribose
(*b*) *a nucleoside*$+H_3PO_4$ → *a nucleotide*

(*ii*) Either β-D—ribose or β-2—deoxy D-ribose. These compounds are pentose sugars. In DNA, the sugar unit is β-2—deoxy-D—ribose, whereas in RNA, it is β-D-ribose.

(*iv*) A phosphate group.

From the pattern of hydrolysis it can be inferred that nucleosides consist of a base linked to pentose. The sugar units of nucleotides making DNA is deoxyribosehence, the name **deoxy ribonucleic acid**. The sugar unit of RNA is ribose, hence, the name **ribonucleic acid**. Two purine bases [adenine(A) and guanine (G)] and two pyrimidine bases [cytosine (C) and thymine (T)] are found in DNA. RNA contains two purine bases [guanine, (G) and adenine (A)] and two pyrimidine bases [uracil (U) and cytosine (C)].

The base and sugar units of nucleosides are held by β—glycosidic linkage from C—1 (or C—1′) of the pentose to N—1 of pyrimidines and N—9 of purines as shown for the deoxyadenosine (deoxyribonucleoside) of DNA in Fig. 16.22.

Ribonucleosides (present in RNA) are also similar to deoxyribonucleosides except that they make use of ribose rather than deoxyribose and uracil replaces thymine.

The nucleotides are the phosphate esters of nucleosides. Phosphate may be linked via the 2′, 3′, 5′ positions of ribose or at 3′, 5′ positions of deoxyribose. All such esters occur. Nucleotide pyrophosphate esters also occur. Such nucleotides are vital energy sources. Adenosine di and triphosphates (ADP and ATP) are the most important of the high energy nucleotides. The terminal phosphate group of nucleotide diphosphates (NDP) and nucleotide triphosphate (NTP) can be selectively removed by specific enzymes with release of energy.

$$\mathrm{R-O-}\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}\mathrm{-O-}\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}\mathrm{-OP} \qquad \mathrm{R-O-}\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}\mathrm{-O-}\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}\mathrm{-O-}\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}\mathrm{-OH}$$

Disphosphate **Triphosphate**

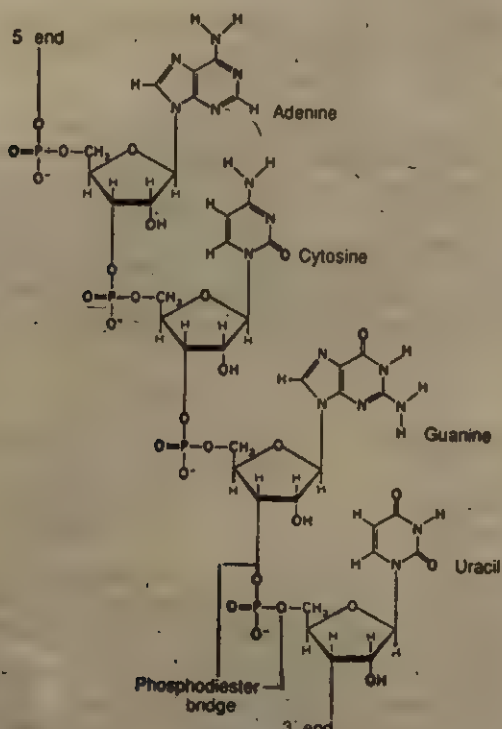
NTP performs number of important functions. They serve as phosphate group carriers for certain reactions. ATP serves as a energy reservoir of the cell and utilized whenever required.

They serve as energy rich precursors of ribonuclotides and deoxyribonucleotides units in the enzymatic biosynthesis of DNA and RNA. During polymerization terminal pyrophosphate groups are released to become the nucleoside monophosphate. Other nucleoside triphosphates include GTA, UTP, CTP, TTP.

16.5.2. Structures of DNA and RNA

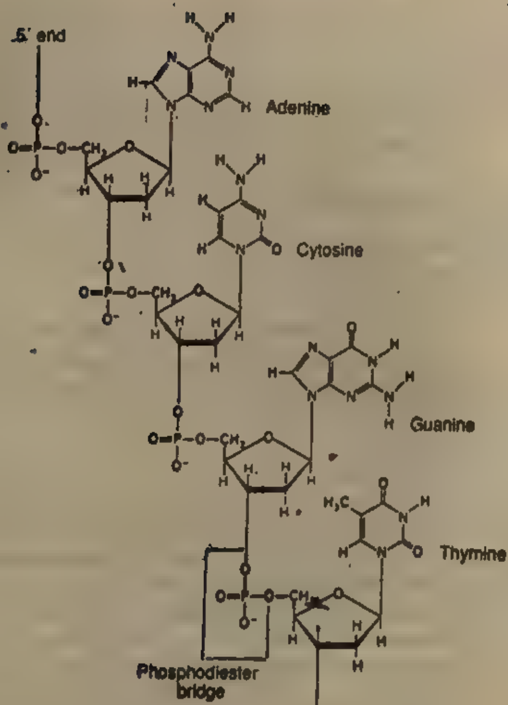
In each macromolecule of nucleic acid, the primary structure of each nucleotide consists of alternating phosphate and sugar units with the four bases protruding from the sugars. The pattern in which the base residues are joined to the sugar phosphate backbone of DNA and RNA is illustrated in Fig. 16.23.

The proportions of the bases and the sequence in which they are arranged along the polynuclotide differ from one kind of nucleic acid to another. J.D. Watson and F.H.C. Crick (1953) on the basis of chemical and X-ray data proposed a structure of DNA, called the secondary structure. DNA consists of two identical polynucleotide chains (or strands) coiled with their heads in opposite direction (*i.e.*, the sugar units are oriented in opposite ways so



(b) RNA molecule

(a)

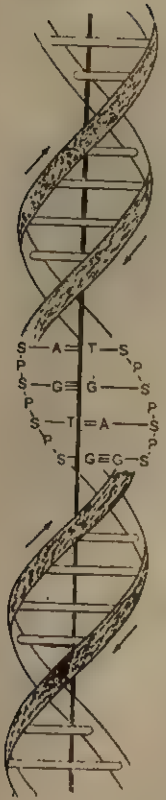


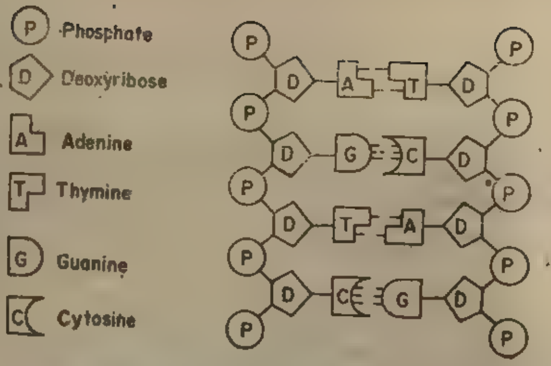
(a) DNA molecule

(b)

Fig. 16.23. Partial molecular structures of DNA and RNA (a) In DNA the structure consists of alternating phosphate and nucleoside units (2 deoxyadenosine, 2-deoxycytidine, 2-deoxy guanosine and 2-deoxythymidine) (b) In RNA the structure consists of alternating phosphate and nucleoside units (adenosine, cytidine, guanosine and uridine).

that the sequence in C-3, C-5 in one strand and C-5, C-3 in the other around same axis to form a double helix (Fig. 16.24). The two strands (*i.e.*, polynucleotide chains) are right handed and have ten nucleotide residues per turn. They are held together by hydrogen bonding between bases, which occupy positions at right angles to the axis of the strands. The hydrogen bonds are formed between the specific nitrogeneous bases of the two strands *i.e.*, two types of hydrogen bonding base pair are present : adenine-thymine and guanine and cytosine. When pairing of bases between two strands (*e.g.*, in DNA) occurs, the strands are said to be complementary to each other.





A representation of a portion of DNA. The bases adenine-thymine and guanine-cytosine are paired together with hydrogen bonds.

Fig. 16.24. (a) The double helix in the DNA. Each strand is antiparallel. The sugar-phosphate chain provides the backbone of each strand. The double helix looks like a ladder, twisted around and around into a cork screw shape, the rungs of which are the hydrogen bonding base pairs : adenine-thymine and guanine-cytosine. Note the sugar-phosphate backbone.

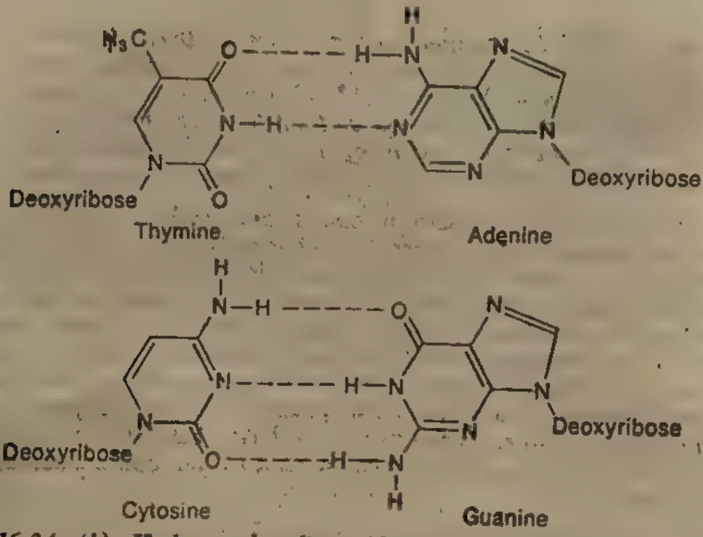


Fig. 15.24. (b) Hydrogen bonding of base pairs in DNA. (Double hydrogen bonding betwenn thymine=adenine ; triple bonding between cytosine≡guanine.

In the secondary structure of RNA, helixes are involved. RNA generally occurs as a single strand of nucleotides connected by phosphate bridges looped back on itself to form or helical structure. In the helical region, the base pairing is possible but the bases present along the loop cannot be paired. RNA molecules vary in size and in a number of loops and helix units.

15.5.3. Biochemical Functions of Nucleic Acids

The nucleic acids are essential for all the life processes. All the biochemical reactions are mediated by nucleic acids. They form genes which are responsible for hereditary character. Thus, they are called the master molecules of life.

Heredity is the term applied to the transmission of potential characteristics of parents to their off spring. Genes are the unit of heredity. All evidences to date suggest that DNA is genetic material and can reproduce a copy of itself. It also serves as a template for RNA synthesis. Each DNA carries enough information to make several different RNA molecules. RNA helps in protein synthesis and depending upon their functions three types of RNA have been recognized, messenger RNA, transfer RNA and ribosomal RNA. Thus two important functions of DNA are recognized : as the repository of hereditary and the director of protein synthesis.

16.5.4. Chemistry and Heredity : The genetic code

Nucleic acids control heredity on the molecular level. The double helix of DNA is the repository of the heredity information of the organism. The necessary information is stored as the sequence of bases along the polynucleotide chain ; it is a message, 'written' in a language that has only four letters A G T C (adenine, guanine, thymine and cytosine). DNA preserves this information and uses whenever required. This could be possible through its two important properties : (*i*) DNA molecules can duplicate themselves, *i.e.*, can bring about the synthesis of other DNA molecule identical with the originals ; this process is called **replication** (*ii*) DNA can control and dictate the synthesis, in an exact and specific way, of the proteins that are characteristic of each kind of organism.

(*i*) Replication (Copying) of DNA

Cell division (undergo mitosis) is necessary for the growth and maintenance of each organism and for the formation of new organisms. During cell division the two strands of DNA separate. Each daughter cell receives one of the two nucleic acid strands. Even though the two strands are not similar, they each contain the information necessary to remake the original dihelical structure. Here, each strand serves as a pattern or template for the formation

of two new strands which will be identical with that originally present in the parent cell (Fig. 16.25).

The new strand molecule is formed by hydrogen bonding with fresh nucleotides present in the nuclear cytoplasm. The newly synthesized DNA molecules again acquire its helical configuration as they are formed. The daughter DNA molecule consists of one old parental strand and one newly synthesized complementary strand. In this way, the exact sequence of bases in the DNA molecule can be retained from parent to daughter cell through many genera-

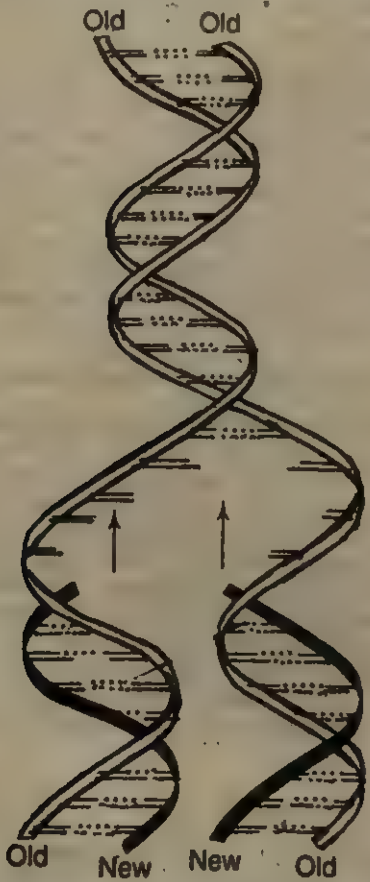


Fig. 16.25. (a) Replication of DNA. The double strand unwinds from one end and complementary strands are formed along each chain. Genetic material of a particular organism in such replication would result in two identical organisms.

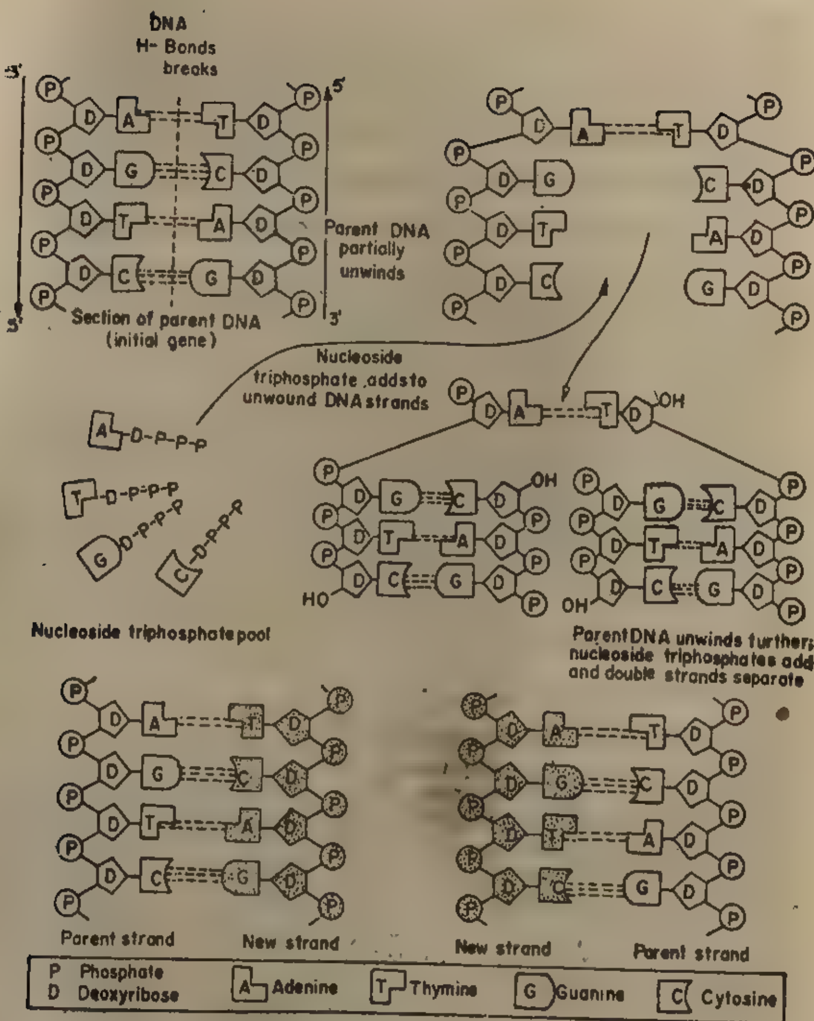


Fig. 16.25. (b) Replication DNA.

tions. All the necessary information required for growth and proper maintenance throughout the life of the cell is stored in the DNA molecule.

Protein synthesis

Ribonucleic acids occur in both the molecules and cytoplasm of all cells.

A section of DNA serves as the pattern for the synthesis of

each RNA. The RNA migrates out of the nucleus into the cytoplasm of the cell. Three distinct types of RNA occur in the cells of higher organisms which are important in protein synthesis :

1. Messenger RNA (*m*-RNA)

2. Ribosomal RNA (*r*-RNA) and

3. Transfer (or Transport) RNA (*t*-RNA)

The *m*-RNA is a complementary copy of a portion of one strand of given DNA molecule. It carries the message given by a DNA molecule for specific protein synthesis. The *r*-RNA provides the site for protein synthesis in the cytoplasm.

The *t*-RNA is responsible for the transport of a specific amino acids to the site of protein synthesis. A little more than twenty different types of *t*-RNA have been identified, each of these *t*-RNA molecules is specific for the transfer of one amino acid.

The genetic information coded in DNA in the language of specific base sequences has to be translated and expressed in the form of synthesis of specific proteins, which perform various functions in the cell. This is carried out in two steps : **transcription** and **translation** (Fig. 16.26).

DNA always works through RNA.

DNA transfers the genetic information to the cytoplasm (where protein synthesis principally occurs) through *m*-RNA which transcribes the genetic code from DNA template to the ribosomes present in cytoplasm *m*-RNA is a copy of DNA and is synthesized enzymatically in the nucleus with DNA as template. The *m*-RNA then diffuses into the cytoplasm, where it becomes attached to the ribosome. At the ribosome, *m*-RNA calls up a series of *t*-RNA molecules, each of which is loaded with a particular amino acid. The order in which the *t*-RNA molecules are called up depends upon the sequence of bases in *m*-RNA. Here amino acids are arranged in the same order as they are to appear in the final protein. The sequence of operations that leads to the synthesis of a polypeptide is summarized in Fig. 16.26 (*b*). The genetic code that directs the insertation of amino acids in the proper sequence in the growing polypeptide chain consists of sets of three bases (called codons). This triplet or codon on the *m*-RNA must be matched by a complementary triplet called an anticodon in *t*-RNA. The specific *t*-RNA with this anticodon carries a specific amino acid to the site of protein synthesis. Each segment of the DNA molecule which codes for a complete protein is called a gene. The DNA present in human cell contains about 5—50 billion nucleotide bases coding for nearly one million genes.

Nirenberg Holey and Har Govind Khorana, through their studies aimed at relating specific codons to specific amino acid units have arrived at the genetic code given in Table 16.5. The significant features of the code are as listed below :

☐ There is more than one triplet code for the amino acids.

☐ The first two letters of the codon are most significant. The third letter varies.

☐ There are several codons that do not represent any amino acids. Although they are referred to as nonsense codons, these seem to play a role in starting and terminating protein synthesis.

☐ The various codons direct the same protein synthesis, whether in bacteria, plants, lower animals, or humans.

The genetic code is presented in Table 16'5.

TABLE 16.5. The genetic code

First base	Second base: U	Second base: C	Second base: A	Second base: G
U	UUU, UUC — Phe UUA, UUG — Leu	UCU, UCC, UCA, UCG — Ser	UAU, UAC — Tyr UAA Nonsense UAG Nonsense	UGU, UGC — Cys UGA Nonsense UGG Trp
C	CUU, CUC, CUA, CUG — Leu	CCU, CCC, CCA, CCG — Pro	CAU, CAC — His CAA, CAG — Gln	CGU, CGC, CGA, CGG — Arg
A	AUU, AUC, AUA — Ile AUG Met	ACU, ACC, ACA, ACG — Thr	AAU, AAC — Asn AAA, AAG — Lys	AGU, AGC — Ser AGA, AGG — Arg
G	GUU, GUC, GUA, GUG — Val	GCU, GCC, GCA, GCG — Ala	GAU, GAC — Asp GAA, GAG — Glu	GGU, GGC, GGA, GGG — Gly

Mutation

The alteration in the arrangement of nitrogenous base arrangement in a DNA molecule is called **mutation**. This alters the *m*-RNA transcribed from it and thereby causes a change in amino acid sequence produced using that *m*-RNA as a template. Changes of DNA molecule can happen spontaneously, or may be caused by radiation, chemical agents, viruses *etc.*

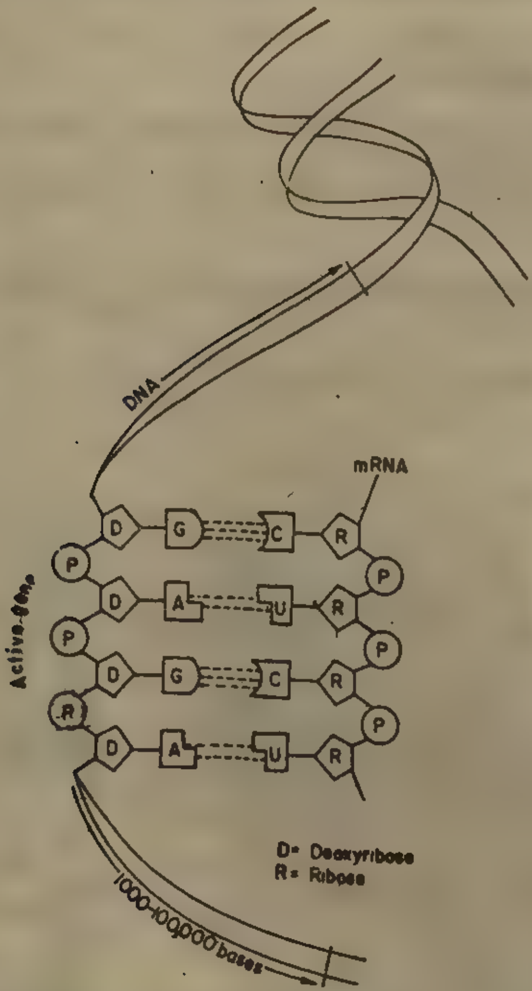


Fig. 16.26. (a) Transcription : Schematic representation. The genetic message coded in the base sequence of DNA is transcribed to a complementary molecule, m-RNA.

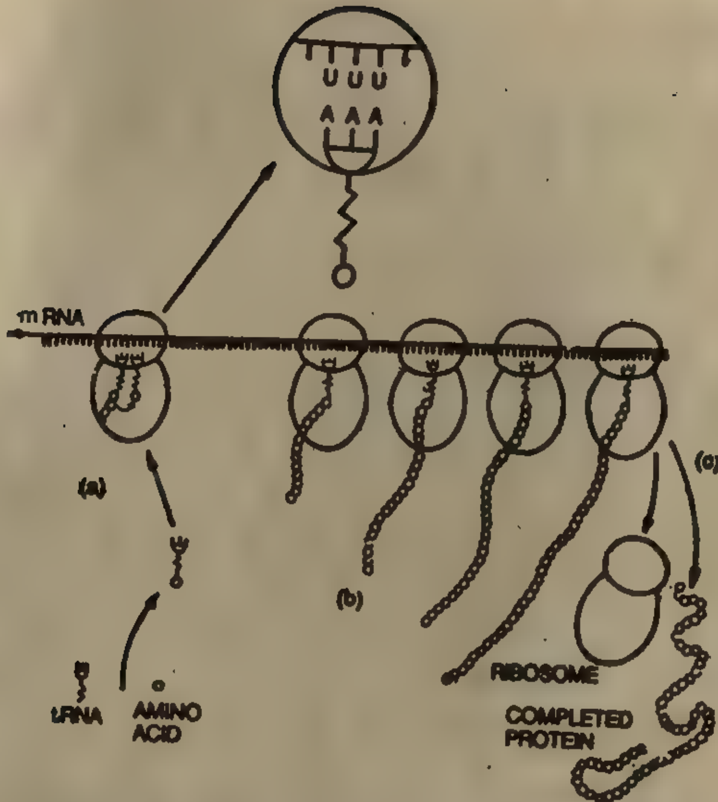


Fig. 16·26. (b) Schematic representation of protein synthesis.

(a) Through the action of an enzyme, a t-RNA molecule brings a single amino acid to a site on a ribonsome. The anticodon of the t-RNA (AAA) as shown must be complementary to the cordon of the m-RNA (UUU). The amino acid joins the chain as shown, the chain moves from the t-RNA on the left to the one on the right,

(b) As the ribosomes move along the m-RNA stand, more and more amino acid units join through the proper matching of t-RNA molecules with the code on the m-RNA,

(c) When the ribosome reaches the end of m-RNA stand, it gets disconnected and releases the completed protein. The ribosome is free to repeat the process.

Perhaps in DNA molecule deletion of base pair takes place.

A—T		A—T
T—A		T—A
G—C	→	| |
G—C		G—C
C—G		C—G
A—T		A—T
C—G		C—G

When this altered gene is replicated, the follow up new genes would be identical to the altered gene.

Most of the changes in DNA can be repaired by special enzymes available in the cell. However, defective repairs carried out by enzymes can cause a mutation. The altered proteins obtained through a mutation invariably have no biological activity. It can cause the death of the cell. The defective genes may cause abnormalities or diseases.

Such diseases are called genetic diseases, *e.g.*, cystic fibrosis, hemophilia and sickle-cell anemia. Such diseases are passed from one generation to the next because of their origin in the DNA.

Denaturation of DNA

Like proteins, the double helix structure of DNA is also affected by certain chemical substances. These reagents interefere with hydrogen bonding between base pairs, charge distribution and other functions. Certain counter ions affect the conformation and flexibility of the polymer. Ions like Na^+ and Li^+ neutralize the negative charge and thus make the conformation of DNA extremely compact. Bivalent cations, such as, Mg^{2+}, Mn^{2+}, *etc.* and diamines present under physiological conditions bond to phosphate and affect conformation extensively. Denaturation (Fig. 16.27) is also effected by heat, certain organic solvents, and variation in pH conditions.

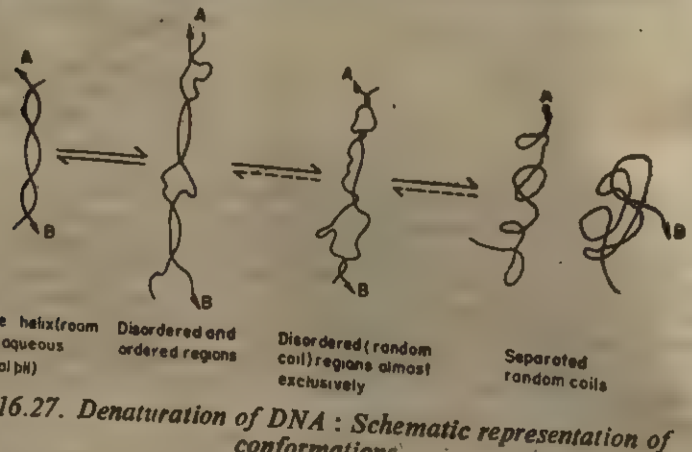


Fig. 16.27. Denaturation of DNA : Schematic representation of conformations

16.6. LIPIDS

Lipids are high hydrocarbon content molecules which are essential constituents of all plant and animal tissues. Cell membranes and brain nervous tissues are particularly rich in lipids. The lipids present in biological tissue may be extracted with non-polar 'fat' solvent. The lipids are a heterogeneous group of organic compounds. Lipids include oils, fats, waxes, cholesterol, some vitamins like D, E,

K and also some hormones like steroid hormones. Thus the lipids have different chemical nature and do not possess common functional groups unlike carbohydrates.

They are classed together because of their solubility in the so called fat-solvents such as, benzene, ether chloroform, carbon tetrachloride, *etc.* Lipids are generally insoluble in water. They are not polymeric in nature *i.e.*, their molecular masses are low. Waxes, triglycerides and phospholipids are the important naturally occurring lipids. They are classified according to their hydrolysis products :-

(*i*) **Simple lipids :** Produce fatty acids and glycerol upon hydrolysis.

(*ii*) **Phospholipids :** Produce fatty acids, glycerol, phosphoric acids and a nitrogen containing compound upon hydrolysis.

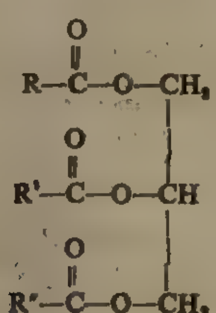
(*iii*) **Steroids :** are compounds having a phenanthrene structure.

Here, we shall briefly describe the features of fats and oils (simple lipids), lecithin (phospholipid) and chlolesterol (a steroid).

16.6.1. Fats and Oils

Fats and oils are esters of gylcerol (a trihydroxy alcohol) and long chain carboxylic acids. These long chain carboxylic acids having even number of carbon atoms are called fatty acids because they occur in fats which is stored in animals and plants. The tri-esters of fatty acids with glycerol are known as triglycerides.

Fats (solids) and oils (liquids) may be represented by the general formula.



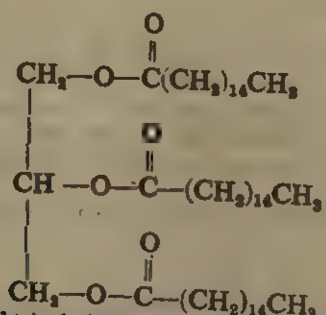
Where R, R′ and R″ may be the same or different groups, and the fatty acid parts $(-\overset{\overset{O}{\|}}{C}-R)$ may be saturated or unsaturated. Fats are the esters of glycerol and generally saturated acids. Oils are

esters that are produced primarily from unsaturated acids and glycerol. The acid part of the fats generally contain an even number of carbon atoms (usually 16 to 18). The acids generally present in fats and oils are

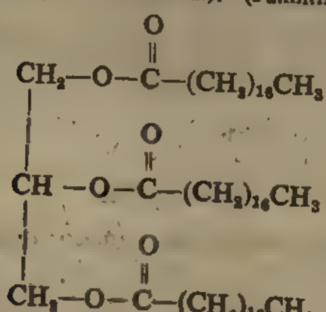
Name	*Structural formula*
Palmitic	$CH_3(CH_2)_{14}COOH$
Stearic	$CH_3(CH_2)_{16}COOH$
Oleic	$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$
Linoleic	$CH_3(CH_2)_4CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$
Linolenic	$CH_3CH_2-CH=CH-CH_2-CH=CH-CH_2-$ $-CH=CH-(CH_2)_7COOH$
Ricinoleic	$CH_3(CH_2)_5CH(OH)CH_2-CH=CH(CH_2)_7COOH$

Naturally occurring fats and oils at times contain different kinds of esters. Milk, ghee, butter, and tallow are some of the familiar fats. Peanut oil, olive oil, soyabean oil, cottonseed oil, palm oil and coconut oil are some of the commonly used oils.

Glycerides are mostly called by their names. The common name is derived from the characteristic stem for the parent acid plus an -in ending.



Glyceryl tripalmitate, a simple glyceride (three R groups are identical). (Palmitin)



Glyceryl tristearate (Stearin)

Fats and oils on hydrolysis by strongly basic solution give salts of the long chain carboxylic acids and the alcohol, glycerol. Salts of fatty acids are termed as soaps. The alkaline hydrolysis of fat is called saponification.

$$\text{Oil (or fat)} + \text{Base} \rightarrow \text{Soap} + \text{glycerol}$$

$$\text{Stearin} + \text{Base} \rightarrow \underset{\text{(a soap)}}{\text{Sodium stearate}} + \text{glycerol}$$

Thus soap is a mixture of the sodium or potassium salts of long chain carboxylic acids—such as, oleic ($C_{17}H_{33}COOH$), stearic ($C_{17}H_{35}COOH$) and palmitic acid.

Waxes are high molecular mass esters—of long chain fatty acids and long chain monohydric alcohols. For example, bee's wax, (from honey comb of the bee) $CH_3(CH_2)_{14}—\underset{\underset{O}{\|}}{C}—O—(CH_2)_{29}CH_3$

and carnabua wax (used in auto and floor polishes) are the esters of myricyl alcohol.

$$C_{27}H_{55}—\underset{\underset{O}{\|}}{C}—O—C_{26}H_{53}$$

They are widely distributed in plants and animals where they frequently serve as protective agents. Wax coating protects surfaces of many plant's leaves from water loss and attack by micro-organisms. Waxes are also used in cosmetics, ointments, and as polishes for floor, furniture, *etc.*

Fatty acids are one of the chief sources of energy in the living cell. Human body makes use of the unsaturated fatty acids to synthesize prostaglindins which are compounds that are found in mammalian tissues and have wide ranging physiological effects. The purgative action of castor oil is due to the presence of a fatty acid, ricinoleic acid.

Triglycerides find use in the manufacture of soaps, paints, varnishes, ointments creams *etc.* They are also used for printing purposes.

The presence of glycerides of unsaturated acids in the daily intake of food prevents the hardening of arteries due to the deposition of cholesterol, and thus reduces the chances of having heart attack *etc.*

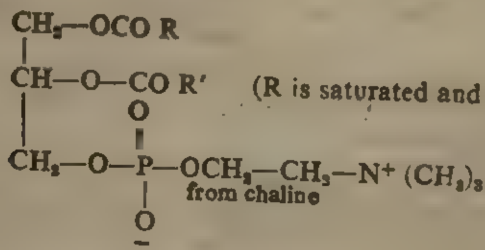
16.6.2. Phospholipids

Phospholipids are abundant in cell membrane, liver, brain and spinal tissues. **They play an important part in many metabolic processes.** In phospholipids, one of the glycerol hydroxyl groups

is esterified with a phosphoric acid derivative while the other two hydroxyls are combined with fatty acids.

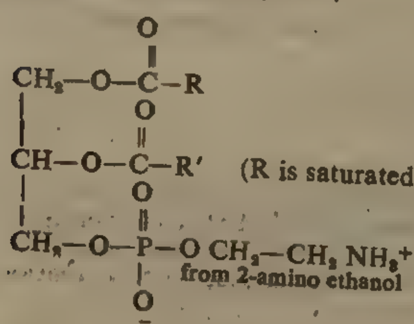
An alcoholic compound that may be choline, ethanol-amine, serine or inositol is also found in them. They are polar in nature.

Thus, the phospholipids, lecithins and cephalins haoc the structure :



(R is saturated and R′ is unsaturated)

Lecithin (choline phosphoglyceride)



(R is saturated and R′ is unsaturated)

Cephalins
(ethanolamine phosphoglyceride)

Lecithins are found in certain foodstuffs, like egg yolk, seeds and soyabeans. They serve useful purpose in the body. They help simple lipids to join with proteins. They play a role in the circulatory transport of fat.

Lipids serve as structural components of cell membranes and are the richest source of energy. Lipids serve as a protective layer when present in subcutaneous tissue of animals.

They resemble soaps in that they are molecules with polar (hydrophilic) and non-polar (hydrophobic) groups. They dissolve in aqueous media by forming micelles. The phosphate group forms a polar, hydrophilic (water-attracting) head on the molecule and the two fatty acid chains constitute the non-polar, hydrophobic (water-repelling) tail. This structure makes the phospholipids as good emulsifying and membrane-forming agents.

Cell Membrane

The cell membranes are constituted mainly of phospholipids and cholines. Their relative proportions vary from cell to cell. The hydrophilic and hydrophobic parts of phospholipids make them perfect molecules suitable for one of their most important biological functions. They form a part of a structural unit that creates an interface between an organic and an aqueous environment. This structure is present in cell walls and membranes where phospholipids remain associated with proteins. They also help in forming the blood clots.

The phospholipids in the membranes appear to be arranged in a double layer or (bilayer) wherein the non-polar tails face each other and the polar heads to the aqueous environment on either side of the membrane (Fig. 16.28).

As illustrated in Fig. 16.28 the proteins found in membrane are either embedded in the bilayer of lipids or attached to either side of the membrane depending upon their functions.

Proteins in membranes help in carrying ions and molecules in and out of the cell. The cell membranes are perfect and selective barriers which allow the nutrients to enter and the waste products to leave the cell. They maintain the shape of the cell. They also help one cell in recognizing the other cells. They also contain receptors for many hormones.

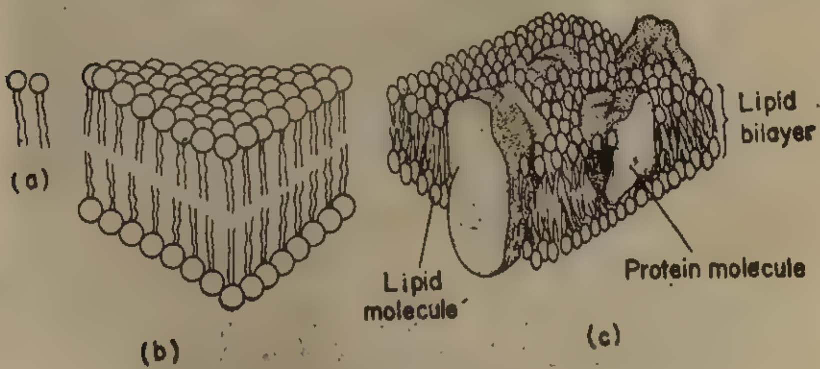
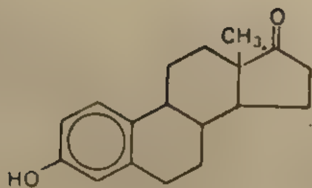


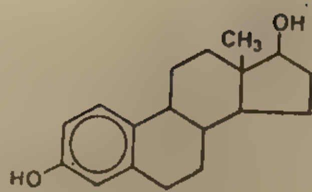
Fig 16·28. (a) Phospholipid molecule.
(b) Lipid bilayer, and (c) Cell membrane.

16.6.3. Steroid Lipids

These lipids are not the esters of fatty acids and glycerol. They are the nonsaponifiable complex substances having unusually high biological activity. Some of the commonly known steroids are given on next page.

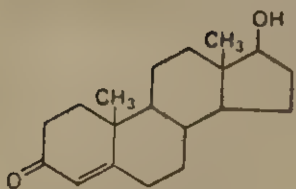


Estrone

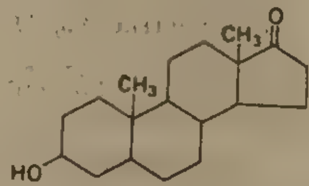


Estradiol

(Female sex hormones)

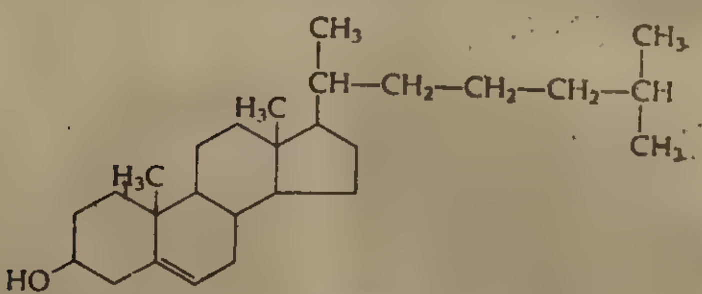


Testosterone

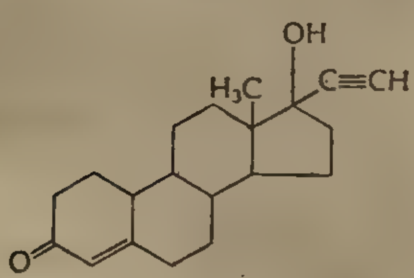


Androsterone

(Male sex hormon)



Cholesterol



Norethindrone : an oral contraceptive

Steroid lipids possess a characteristic cyclic structure, called a steriod nucleus. Cholesterol is the most abundant steroid in the human body. Clinical investigations have established that there is a correlation between the cholesterol level in the blood and incidence of heart attacks and atherosclerosis. Some steroids also act as vitamins and hormones.

16.7. CHEMICAL EVOLUTION, ORIGIN OF LIFE

It is interesting to speculate on the possible origins of life. It has been one of man's great yearnings and has enriched his religious life. There have been existing two strong beliefs : **divine creation** and **spontaneous generation**. In recent years, spontaneous generation in the prebiotic earth received lot of support on the basis of evidences.

In the beginning of 20th century, a Russian biochemist, A.I. Oparin advanced some ideas which based on rocky nature of the earth with a good deal of liquid surface water and an atmosphere with CH_4, NH_3, H_2 and water vapour. High temperature conditions initiated the process of vaporization and condensation of water and hence probability resulted in torrential rain and electrical storms over the earth's surface. There was no free oxygen and no layer of ozone to absorb ultraviolet radiation from the sun. Moreover, the abundance of radioactive isotopes in the prebiotic earth could also provide enough and constant supply of energy. It is reasonable to assume that under such conditions no life could exist. However, under such conditions—an atmosphere of completely hydrogenated carbon, N_2, O_2 and different sources of energy (*i.e.*, ultraviolet, electrical discharges and nuclear radiation)—the synthesis of many simple organic molecules (*e.g.*, HCN, HCHO, ...) could occur, which, later on, gave rise to simple self-duplicating molecules and cells and ultimately a complex variety of life on the earth.

It was expected that simple molecules-HCHO, HCN, *etc.* reacted further in aqueous conditions to produce amino acids, sugars, nucleotides and fatty acids essential for the synthesis of proteins and thus for cells.

Many experimental evidence strogly supports the possible formation of many simple molecules in the early earth. Thus it appears to be a very long way from such simple organic molecules to the highly complex bioorganic substances of living cells. From the time life could have originated on the earth, enormous time have passed In this period, the earth had cooled sufficiently to sustain life. Even the most improbable events can be expected to occur with great certainty.

Evolution is a naturally occurring process. It is a slow, continuous and irreversible process of change. Evolution occurs through variations arising from changes in genetic material and from natural selection.

All living organisms are made up of nearly the same elements that have cells as their structural units. They derive their energy from their environment and synthesize the building blocks of their macromolecules. Raw materials (nutrients taken into the cell) are disassembled and reassembled into products used to help the cell grow, to repair the cell, to make new cells, and to produce energy. All such processes involve chemical reactions called **metabolism.** Metabolism, replication and homeostasis are the three characteristics of the living organisms. In spite of this common natural phenomena, nature is full of diverse forms of life, ranging from bacteria to human beings and from di-atoms to trees.

Although a variety of foods is employed by the various kinds of cells. They all derive their fundamental food from one fundamental chemical process **photosynthesis.**

$$6CO_2+6H_2O+\text{energy} \xrightarrow[\text{Chlorophyll}]{h\nu\ \text{(plants)}} C_6H_{12}O_6\ \text{(energy)}+6O_2$$

This is the series of chemical reactions through which green plants convert atmospheric CO_2, and water vapour into carbohydrate molecules and in the process transform the sun's energy into chemical energy.

Cells, likewise, carry out an energy releasing operation in a controlled way, for example, food molecules like carbohydrates, fats, *etc.* combine with oxygen through a series of intermediate steps producing CO_2, H_2O, and energy.

$$C_6H_{12}O_6+6O_2 \longrightarrow 6CO_2+6H_2O+\text{energy}$$

The energy liberated is stored in the form of relatively unstable covalent bonds in special molecules to be used in the subsequent energy consuming processes of the cell.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

16.1. Choose the correct answer of the four alternatives given for the following questions :

(*i*) Which of the following is not a disaccharide ?

(*a*) lactose (*b*) ribose

(*c*) maltose (*d*) sucrose

(*ii*) Cane sugar on hydrolysis gives

(*a*) glucose and sucrose

(*b*) glucose and ribose

(*c*) glucose and fructose

(*d*) only glucose.

(*iii*) Which of the following is a globular protein ?

(*a*) haemoglobin (*b*) fibroin

(*c*) collagen (*d*) keratin

(*iv*) Which of the following is a polar amino acid ?
(*a*) lysine (*b*) tyrosine
(*c*) leucine (*d*) glycine

(*v*) Which of the following is not found in DNA ?
(*a*) adenine (*b*) guanine
(*c*) thymine (*d*) uracil

(*vi*) Invert sugar is a mixture of
(*a*) glucose and fructose
(*b*) lactose and sucrose
(*c*) galactose and ribose
(*d*) fructose and galactose

(*vii*) Which of the following is a linear polymer ?
(*a*) cellulose (*b*) starch
(*c*) amylopectin (*d*) glucogen

(*viii*) Which of the following compounds do not belong to lipids ?.
(*a*) wax (*b*) fat
(*c*) myglobin (*d*) cholesterol

(*ix*) Nucleic acids are the macromolecules of
(*a*) nucleotide (*b*) nucleoside
(*c*) adenosine (*d*) thymine

(*x*) Oils and fats are the
(*a*) phospholipids
(*b*) esters of alcohols
(*c*) glycerides of higher fatty acids
(*d*) none of the above

16.2. Fill in the blanks :

(*i*) A carbohydrate containing six carbons and an aldehyde group is classified as an............

(*ii*) The carbohydrate that makes up the fibrous parts of plants is called............

(*iii*) Hydrolysis of proteins yields............

(*iv*) Amino acids in poteins are joined together by............

(*v*) Hydrolysis of a fat molecule yields one molecule of............and three molecules of..........

(*vi*) The sex hormones are lipids of the.........type.

(*vii*) Ribose and deoxyribose are called.........

(*viii*) Protein loses its.........activity on denaturation.

(*ix*) The proteins are the.........polymers of amino acids.

(*x*) An.........is a catalyst produced by a living cell.

16.3. State which of the following statements one true (T) and false.(F) :

(*i*) Hydrolysis of milk sugar yields one molecule of each glucose and fructose.

(*ii*) Amylose is made of long, unbranched chains of glucose.

(*iii*) Cellulose is a polysaccharide of fructose.

(*iv*) The amino acids in a protein are joined in a distinct sequence.

(*v*) The structure and functioning of a human body depends primarily on proteins.

(*vi*) All lipids are esters.

(*vii*) DNA is found in the cytoplasm.

(*viii*) DNA strand serves as a template for the formation of a complementary strand.

(*ix*) *t*-RNA carries specific genetic information from the chromosomes to the ribosomes.

(*x*) RNA is synthesized in the nucleus under the control of DNA.

SHORT ANSWER QUESTIONS

16.4. Give answers of the following questions briefly :

1. Name the products which maltose, sucrose and lactose give on hydrolysis.
2. What is photosynthesis ?
3. What is a glycoside bond ?
4. What is saponification ?
5. What is hydrogenation ?
6. Translate the following base sequence abbreviations :
   (*a*) A—C—G—H, and (*b*) T—A—G—C
7. Giving the source, state some of the important uses of the following :
   (*a*) starch (*b*) cellulose
8. Differentiate between an amide and peptide bond.
9. What are the important functions of proteins in the body ? Give illustrations.
10. Name the process which is related to unfolding to peptide chain. What does happen after the peptide chain unfold ?
11. How does DNA differ from RNA ?
12. To which class of the compounds the following compounds belong Guanine, thymine, uracil, triglyceride, wax, maltose, sucrose, invertase, yeast, pepsin galactose, lecithin, cholesterol, cytosine
13. What is the nature of bond in DNA ?
14. What will be the base sequence for the complementary RNA strand when the DNA base sequence is as given,
    A—T—G—C—T—A—T—A
15. Name the products which are produced when wax is hydrolyzed ?

TERMINAL QUESTIONS

16.1. Name the building materials of cell ? What are its functions ?

16.2. (*a*) What are carbohydrates ? How are they classified ?

(*b*) Is the name representative of their properties ?

16.3. What is a disaccharide ? How does it differ from polysaccharide ?

16.4. What functions do the carbohydrates serve in living organisms ?

16.5. Compare the structures of starch and cellulose. Give the chief differences between the two.

16.6. (a) Write the linear and ring forms of sugar.

(b) Give an example of each of the following :

(i) a hexose
(ii) an aldohexose
(iii) a ketohexose
(iv) a furanose
(v) a pyranose

16.7. Glucose, galactose and fructose have the same molecular formula $C_6H_{12}O_6$. In what way these three carbohydrates are different from another ?

16.8. Why is it that human beings can digest starch but not cellulose ?

16.9. What role do carbohydrates play in living systems ?

16.10. What is meant by the term 'essential' amino acids ?

16.11. What are proteins ? Do they have amide linkages ?

16.12. Describe the primary and secondary structures of proteins.

16.13. What is meant by the term 'denaturation of a protein' ?

16.14. State differences between the following :

(i) A globular protein and a fibrous protein
(ii) Primary and secondary structure of a protein
(iii) α-Helix and β-pleated sheet configuration

16.15. What type of bonding occurs in

(i) α-helix configuration,
(ii) globular proteins,
(iii) β-sheet ?

16.16. State the four functions of proteins in a living organism.

16.17. What is meant by tertiary structure and quaternary structure ? How do the properties of solvent affect these structures of poteins ?

16.18. What are enzymes ? How do they work ? Explain. What are their characteristics ?

16.19. Name the enzymes useful for the fermentation of starch to alcohol.

16.20. What are nucleic acids ? Do they differ from proteins in their chain structure ?

16.21. (a) What do the terms RNA and DNA stand for ? State the difference between the two.

(b) Mention three types of RNA molecules in a cell. Give functions of each.

16.22. Describe briefly the double helix structure of DNA. Give the functions of DNA.

16.23. Pick out the naturally occurring compounds from the following : starch cellulose, α-amino acids, uracil, thymine, PVC, teflon polythene and urease.

16.24. Define the following terms :

(a) lipid
(b) nucleic acid
(c) carbohydrate
(d) enzyme, and
(e) protein

16.25. Describe the genetic code for nucleic acids. Define the terms gene, triplet, codon and anticodon.

16.26. Describe the structure of a nucleotide. What is the difference between the nucleotide units in DNA and RNA ?

16.27. What occurs with DNA during cell division ? How is the DNA replicated ?

16.28. What holds the two DNA strands together in the double helix. Illustrate the base pairing between C and G ; T and A.

16.29. What are the various functions of nucleic acids ?

16.30. How is DNA able to duplicate itself ?

16.31. (*a*) Explain the essential difference between the following pairs of materials.

(*i*) A fat and a lipid
(*ii*) a fat and an oil and
(*iii*) a fat and a wax.

(*b*) Explain, why do phospholipids dissolve readily in water than simple or mixed glycerides.

16.32. Describe what is meant by each of the following terms :

(*a*) amino acid (*b*) peptide bond
(*c*) polypeptide (*d*) protein
(*e*) N-terminal amino acid (*f*) α-helix
(*g*) denaturation (*h*) asymmetric carbon atom, and
(*i*) chiral centre.

16.33. What are the principal functions of each of the following in protein synthesis :

(*a*) DNA, (*b*) *m*-RNA and
(*c*) *t*-RNA ?

16.34. (*a*) What are lipids ? How are they classified ?

(*b*) How does a phospholipid differ form triglyceride ?

16.35. What is heredity ? What is genetic disease ? Is it fatal to the organism ?

16.36. What is cell membrane ? Explain the role of lipids in the context of cell membrane ? What are the functions of the cell membrane ?

ANSWERS TO SELF ASSESSMENT QUESTIONS

16.1. (*i*) (b) (*ii*) (c) (*iii*) (a) (*iv*) (b) (*v*) (d)
(*vi*) (a) (*vii*) (a) (*viii*) (c) (*ix*) (a) (*x*) (c)

16.2. (*i*) aldohexose (*ii*) cellulose
(*iii*) amino acids (*iv*) peptide bond
(*v*) glycerol, fatty acids (*vi*) steroid
(*vii*) pentoses (*viii*) biological
(*ix*) condensation (*x*) enzyme

16.3. (*i*) F (*ii*) T (*iii*) F (*iv*) T
(*v*) T (*vi*) F (*vii*) F (*viii*) T
(*ix*) F (*x*) T

16.4. (*i*) Maltose + H_2O $\longrightarrow$ glucose and glucose

(*ii*) Sucrose + $H_2O \longrightarrow$ glucose and fructose

(*iii*) Lactose + $H_2O \longrightarrow$ glucose and galactose

2. Photosynthesis is a complex series of chemical reactions. In the sunlight, chlorophyll absorbs energy. Photolysis of water produces hydrogen which can reduce CO_2 giving glucose.

3. Linkage produced by the elimination of water when two simple sugars combine.

4. Saponification is the name given to the hydrolysis of fats or oils by a strong base.

5. It is a process of adding hydrogen across the double bond. Vegetable ghee is produced by hydrogenation.

6. (*a*) This is a strand of RNA. A—C—G—U.
Adenine—Cytosine—Guanine—Uracil

(*b*) This is a strand DNA. T—A—C—G
Thymine—Adenine—Cytosine—Guanine

7. (*i*) **Starch Source :** Cereals, potatoes, legumes

Use : (1) source of food. (2) Rich source of carbohydrate. (3) manufacture ethanol

(*ii*) **Cellulose Source :** Wool, wood, cotton

Use : (1) wood as source of cellulose is used for building and furniture (2) cotton is used in the manufacture of threads, fabrics, *etc.* (3) a good source of glucose (4) Esters of cellulose are used to make varnishes, man made fibres, *etc.*

8. An amide linkage is formed by the elimination of water molecule when a carboxylic acid combines with an amino group.

$$R-\underset{\underset{O}{\|}}{C}-OH+H-\underset{\underset{H}{|}}{N}-R' \longrightarrow R-\underbrace{\underset{\underset{O}{\|}}{C}-NH}_{\text{Amide bond}}-R'+H_2O$$

A peptide link is formed by the elimination of water when two α-amino acids combine.

$$H_2N-\underset{\underset{R}{|}}{CH}-COOH+H_2N-\underset{\underset{R'}{|}}{CH}-COOH \rightarrow H_2N-\underset{\underset{R}{|}}{CH}-\underbrace{CONH}_{\text{Peptide bond}}-\overset{\overset{R'}{|}}{CH}-COOH$$

The peptide bond (—CONH) involves the α-amino and α-carboxylic groups of α-amino acids. More amino acids may be added to a peptide.

9. 1. Helps in storing oxygen in muscles until it is required for energy production—Myoglobin

2. A carrier of oxygen from lungs to various tissues through blood stream—Haemoglobin.

3. Helps in enhancing the rate of biochemical reactions—carbonic anhydrase, maltose, yeast, *etc.*

10. Denaturation

It spoils the tertiary structure of proteins which results into a loss of biological activity. The protein becomes insoluble. Denaturation is caused by heat, acids, high salt concentration of heavy metals.

11. DNA=the nucleotide of DNA involves deoxyribose (sugar) and one of the four bases, i.e., thymine (T), Cytosine (C), guanine (G) and adenine (A)

RNA=the nucleotide of RNA involves ribose (sugar) and one of the four bases, *i.e.*, uracil (U)., cytosine (C), guanine (G) and adenine (A),

12. **Purine** : Guanine, Cytosine,

Pyrimidine : thymine, uracil,

Lipid : triglyceride, wax, lecithin, cholesterol,

Protein : Invertase, yeast, pepsin,

Carbohydrate : maltose, sucrose, galactose.

13. The two strands of the DNA are held together by hydrogen bonds between specific base pairs. A is linked to T through two such bonds whereas G bonds to C with three hydrogen bonds.

14. Sequence of the other strand is

T—A—T—A—G—C—G—C

15. Wax on hydrolysis gives long chain fatty acids and long chain alcohols.

□·□

UNIT 17

Chemistry of Biological Processes

Nature set herself the task to catch in flight the light streaming towards the earth, and to store this, the most evasive of all forces, by converting it into an immobile form. To achieve this she has covered the earth's crust with organisms, which while living, take up the sunlight and use its force to add continuously to a sum of chemical difference.

J.R. VON MAYER (1845)

UNIT PREVIEW

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Comment on the various aspects of biological processes.
2. Describe a living cell and its primary functions.
3. Emphasize and understand the importance of the macromolecules for our living system.
4. Explain the importance of the terms : metabolism, digestion, respiration. photosynthesis.
5. Explain the various aspects of cellular energetics.
6. Emphasize the importance of water and blood.
7. Appreciate the immune system response in the context of cell defence.
8. Describe the importance of hormones and vitamins for the living system.
9. Describe the causes of various diseases and their prevention.

17.1. INTRODUCTION

The cell, commonly considered to be the simplest self-sustaining living unit, can be thought of as analogous to a large chemical factory in which many raw materials are introduced and converted into many products. Each cell is characterized by an outer membrane whose function is to contain the highly organized chemical system and to monitor the influx of substances required. There are several organelles present in the cellular fluid or cytoplasm contained in the cell membrane. The two of the several organelles—the nucleus and the mitochondria—are the focal point of all the biochemical processes. The totality of the reactions taking place in an organism is referred to as metabolism. Metabolism describes essentially two chief operations :

1. Chemical reactions that occur in the transformation of food molecules into smaller ones and into CO_2 and H_2O with the liberation (or generation) of chemically usable energy. The sum total of all such reactions is called **catabolism.**

2. Chemical reactions which help in synthesizing the complex molecules like proteins, carbohydrates, fats, and nucleic acids necessary in carrying out the functions of the cell. Such reactions are given the name of **anabolism.**

The catabolic reactions serve to provide both energy for various cellular functions as well as the starting materials for anabolism. The process of synthesis and degradation are not simply reverse of each other and may occur by different chemical paths. Together, the synthesis and degradation constitute **Metabolism.**

A large portion of the energy released is stored as chemical energy in compounds such as nucleoside triphosphates. These compounds, in turn, react with water releasing energy. This energy is utilized by the cell for functions or chemical reactions other than catabolic and anabolic reactions, *i.e.*, for muscular contraction and locomotion, initiating chemical reactions to produce structural and functional components of the cell, carrying substances across membranes, transmission of nerve impulses, growth, maintenance and repair of the cell, *etc.*

17.2. CELL METABOLISM

The cells have a fluid medium called intracellular fluid formed of cytoplasm, and a fluid surrounding them called **'Extracellular fluid' (ECF).** The ECF forms an immediate environment to the cells. The human cells are bathed in an interstitial fluid derived from the blood. Living cells are found inside the body below the skin, while the cells on the outer surface of the skin are dead cells. The cells react with the ECF and there is adjustment of the cells to the ECF.

Composition of ECF

Water is the major component of ECF in which contain dissolved molecules and ions of gases and substances.

1. Gases : Oxygen and carbon dioxide (major ones).
2. Inorganic ions : Na^+, K^+, Cl^-, Ca^{2+}, HCO_3^- and PO_4^{3-} (in substantial amounts)
   Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, F^- (in trace amounts).
3. Amino acids, sugars and lipids (cellular food)
4. Vitamins (perform special metabolic work as in prosthetic group of enzymes).
5. Hormones (present in multicellular organism).
6. Excretory wastes (sent from the cell in the form of ammonia, urea, *etc.*)

The pH and the temperature of the ECF are of vital importance to the cells as ECF forms their immediate surrounding. In humans, the pH is maintained between 7.3 and 7.4 and the temperature around 37°C (98 6°F) fluctuating within a degree. The physiological processes of multicellular organisms are maintained by the composition of ECF kept within narrow limits. This results in maintaining the constancy of the internal environment called **homeostasis**. The homeostatic control has reached the maximum efficiency in the birds and mammals which is due to the specialization of cells.

Cell metabolism involves the following :

1. All the requirements for the cells are obtained from the ECF and the products and the waste materials of the cells . are sent into ECF. Thus there is material exchange between the cell and the ECF. The nutrients absorbed by the cells from the ECF constitute cellular nutrition.

2. Cellular metabolism involves digestion, respiration and fermentation by which the complex food material is broken into simpler products. The enzymes take part in these reactions.

3. When the nutrient molecule is inside the cell, it under goes cellular respiration for release of energy or to form the building blocks of macromolecules of the cell resulting in metabolic synthesis.

Thus a cell requires a constant source of energy to carry out its multifarious processes. A cell maintains its strict control over its functioning to achieve high efficiency. In this unit, the discussion centres on the simple aspects of cellular energetics, meta-

bolism and the chemical basis of some important biological processes.

17.3. CELLULAR ENERGETICS (Bioenergetics)

An organism is an efficient isothermal engine. Without requiring any flow of heat, it utilizes a high percentage of the free energy available form its nutrients to perform various mechanical work. Moreover, the cell operates at constant temperature.

A key requirement of various chemical reactions is that they be spontaneous in a thermodynamic sense *i.e.*, ΔG must be negative. Reactions for which the standard free energy is negative are **exergonic**, and those for which it is positive are **endergonic**.

Thus,

(*i*) When $\Delta G<0$, the process is exergonic and thermodynamically spontaneous.

(*ii*) When $\Delta G>0$, the process is endergonic and thermodynamically non-spontaneous.

Cells carry out many energy liberating reactions, *e.g.*, carbohydrates and fats combine with oxygen through a series of intermediate steps and finally give CO_2, H_2O and energy (or $-\Delta G$). This process occurs in the mitochondria. There are some other reactions particularly anabolic reactions which need energy and hence are not spontaneous (*i e.* $+\Delta G$). Non-spontaneous reactions can proceed smoothly in combination with reactions for which ΔG is quite high and negative. For example, consider two reactions,

(*i*) Glucose (G)+H_3PO_4 (P)—G-6-P+H_2O $\qquad \Delta G^\circ=+12.5$ kJ mol^{-1}

(*ii*) $ATP+H_2O \rightarrow ADP+H_3PO_4 \qquad \Delta G^\circ=-31.4$ kJ mol^{-1}

The reaction (*i*) is thermodynamically non-spontaneous and the reaction (*ii*) is a spontaneous process. When these two reactions are coupled, the overall reaction becomes spontaneous *i.e.* ΔG° for the reaction is negative

$$\text{Glucose}+\text{ATP}\rightarrow\text{G-6-P}+\text{ADP} \qquad \Delta G^\circ=-18.9 \text{ kJ mol}^{-1}$$

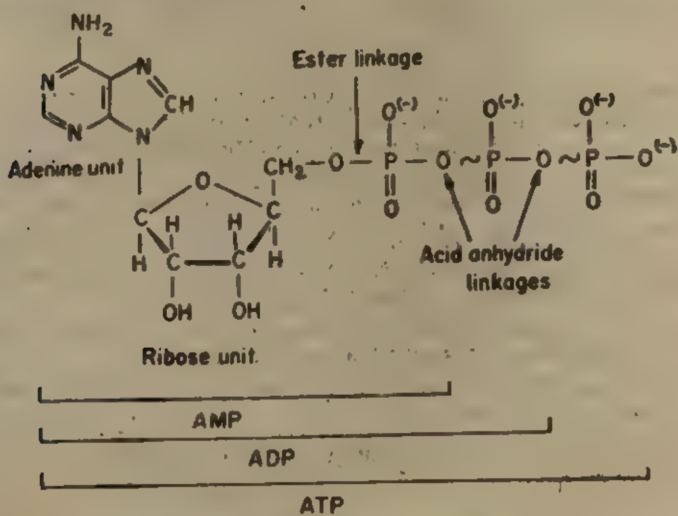
Similarly the synthesis of protein from amino acid, a endergonic reaction is driven by hydrolysis of ATP to ADP. Thus, all energy requiring cellular reactions proceed successfully on coupling with energy releasing reactions. It has been found that a cell uses ATP as an intermediate storehouse of metabolic free energy. The conversion of ATP to ADP provides the required energy.

17.3.1. Adenosine Triphosphate (ATP)

The P-O-P link present in ATP is very important in the

chemistry of biologically active molecules as it is the prime store of energy in biological systems. The energy of the bond is allegedly released to the system by hydrolysis of the P-O-P link in adenosine triphosphate, ATP, the so-called high energy phosphate.

ATP consists of a purine-base component, adenine-attached to D-ribose molecule-together forming a nucleotide, which is universally found in cells. The formation of ATP molecule is termed as **oxidative phosphorylation**



The symbol ~ designates high energy bonds

The anion ATP^{4-}, present in high concentrations in all cells, is decomposed by water to ADP^{3-} and inorganic phosphate—($P_i = HPO_4^{2-}$)

(17.1)......$ATP^{4-} + H_2O \rightarrow ADP^{3-} + P_i + H^+ \quad \Delta G^\circ = -38.85 \text{ kJ mol}^{-1}$

(17.2)......$ATP^{4-} + H_2O \rightarrow AMP^{2-} + P_i + H^+ \quad \Delta G^\circ = -42.47 \text{ kJ mol}^{-1}$

Where ADP^{3-} and AMP^{2-} are adenosine diphosphate and adenosine monophosphate anions respectively. The value of ΔG° depends upon the pH of the medium.

From the hydrolysis reaction it is clear that the association of ATP^{4-} hydrolysis with important reactions in living systems is thermodynamically sound, *i.e.*, ΔG° for such hydrolysis reactions are quite large. Both the reactions (17.1, 17.2) are nearly the same thermochemically and both appear to be favourable with respect to hydrolysis of the ester group. It is fairly easy to convert ADP to

ATP. Many metabolic reactions yield the free energy required for synthesizing ATP from ADP and phosphate. The coupling of the ATP hydrolysis (energy releasing) reactions with energy needing reactions in a cell proceeds through one or more steps of phosphate or nucleotide transfer to the other reagent. In addition, an enzyme always catalyzes the intermediate reactions or helps in deciding the hydrolysis reactions (either 17.1 or 17.2).

The formation of these energy rich phosphate compounds, which occurs in the cytoplasm of the cell, represents an important mechanism for extracting energy from the metabolism of foodstuffs.

Now at this stage one is forced to think about the ultimate source of the energy-rich molecules that organisms use to fulfill the need of anabolic reactions and do the other work of staying alive. Cells synthesize such molecules, like glucose from simpler precursors at the expense of breaking down other energy-rich substances.

The energy for all such processes ultimately comes from the sun. In a broad sense, the energy is transferred into ATP molecules by two series of chemical reactions :

1. the photosynthesis process, in which the solar energy is converted into chemical energy in glucose bonds.

2. the cellular oxidation of glucose in which the energy in glucose is transferred to ATP.

The overall process may be portrayed in Fig. 17.1.

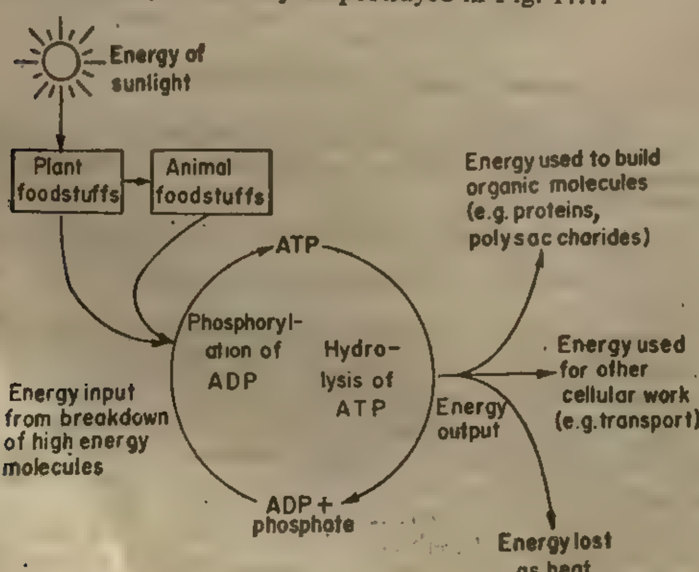


Fig. 17.1. The flow of energy through the living world

17.4. PHOTOSYNTHESIS

The energy for life ultimately comes from the sun. Nuclear reactions that occur all the times in the sun are a source of enormous amount of energy. This radiant energy from the sun is captured by plants growing on earth and by certain bacteria, to produce organic molecules such as carbohydrates and amino acids. This process of conversion of solar energy into chemical energy is called **photosynthesis**. It is performed by green plants and many one-celled organisms. It keeps the life on earth going.

Photosynthesis takes place in regions of the plant cells called **chloroplasts**. These chloroplasts contain the highly organised systems of pigments, electron carriers, and enzymes necessary for photosynthesis in green plants.

Photosynthesis is a complex series of chemical—'light and dark' —reactions. In the primary light reaction, the chlorophyll captures photons of sunlight, which, in turn, is utilized to synthesize energy-rich molecules (ATP) and O_2 and NADPH [Reduced product of nicotin amide adenosine dinucleotide phosphate]. The dark reactions then use these energy-rich molecules to convert atmospheric carbon dioxide into glucose and storage molecules such as starch or cellulose.

Enzyme NADPH acts as a reducing agent, *i.e.*, required for the biosynthesis of glucose, *etc.* The overall process of photosynthesis can be understood as given in Fig. 17.2.

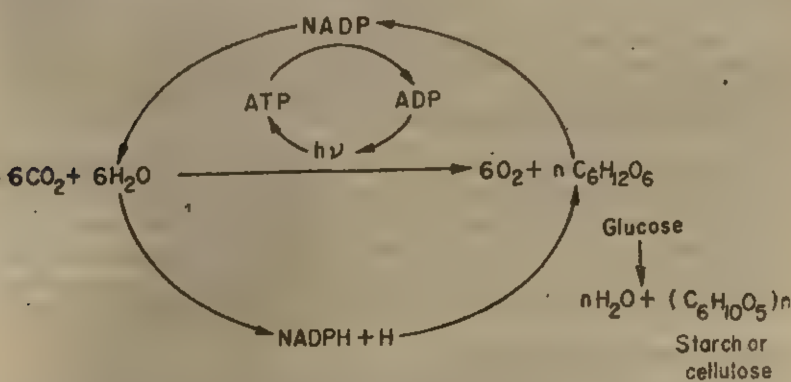


Fig. 17.2. Simplified scheme of photosynthesis.

The cells which derive their energy as photons from the sun are called **phototrophs** (present in plants, algae and certain bacteria such as Halo bacteria). These cells use the chemical energy acquired

in the course of photosynthesis to synthesize carbohydrates, proteins, nucleic acids and other nutrients required for the cell growth, maintenance and reproduction.

Other forms of life for example, animals, humans are chemotrophs. Chemotrophs derive chemical energy for cellular activities by consuming the organic molecules produced by photorophs and break them down to simple molecules by a process which is known as **digestion**.

17.5. DIGESTION

The metabolism of nutrients contained in the cell forms ATP. Therefore it is essential for the nutrients to be digested and absorbed into blood-steam before ATP can be synthesized. In digestion, the complex foods are broken down into simple molecules. In mammals, the digestion of food occurs with the help of several enzymes mainly in mouth, stomach and small intestine.

17.5.1. Carbohydrate Digestion

The digestion of carbohydrates starts in the mouth through the action of salivary enzymes, the amylases ; starch is hydrolyzed to maltose and a group of carbohydrates known as dextrins. From here the food goes to stomach where the pH is 2.0. At this pH, the enzyme amylase becomes inactive, and hence, the digestion process stops. From stomach the food passes over to small intestine where it gets mixed with enzymes secreted by the pancreas and cells in the lininig of intestine. These enzymes complete the hydrolysis of polysaccharides to monosaccharides such as glucose, fructose and galactose.

These monosaccharides pass through intestinal walls into the bloodstream and to the liver. The enzymes contained in liver convert galactose into glucose. Fructose is either converted to glucose or used as such for various purposes.

Some polysaccharides, *e.g.*, cellulose which constitute our diet do not provide energy because there are no enzymes to digest them. However, cellulosic fibre ingested with diet helps in normal functioning of the large intestine by providing the necessary roughage. Grazing animals also do not have a correct digestive enzyme for cellulose but they depend on intestinal bacteria which have cellulose.

17.5.2. Digestion of Proteins

Proteins get hydrolyzed into amino acids before they are absorbed into the bloodstream. The digestion of proteins occurs in the stomach and small intestine. The fluid in stomach is acidic (pH$\sim$2) as the gastric juice secret enough HCl to make it acidic. Acidic conditions in the stomach help in the denaturation of pro-

teins. Here, HCl and the enzyme **pepsin** (protease) break protein into small units of polypeptides. Now when the food goes to intestine, **peptidases** such as trypsin and chymotrypsin (from the pancreas) and others cleave the small polypeptide units into amino acids. These amino acids pass through the wall of the intestine into blood stream and on to various organs.

17.5.3. Digestion of Lipids (fats and oils)

The digestion of fats and oils occurs primarily in small intestine where almost all the favourable conditions (pH 7.5) exist, through the action of a combination of lipase enzymes (from the pancreas). Here, the fats, *etc*. first gets mixed with bile fluid (from liver). This emulsifies fats (*i.e.*, disperses the big molecules into small ones) and checks the growth of bacterria. Now in the presence of pancreatic lipase (steapsin) fats hydrolyzes into glycerol, mixtures of mono- and diglycerides and fatty acids, which pass into the bloodstream through the walls of the intestine.

17.6. RESPIRATION

The energy needed by cells is obtained from the oxidation of complex organic molecules by **cellular respiration.** Oxidation of the organic compounds consumed as nutrients takes place in step so as to release energy in a controlled fashion. A part of the energy so released is used in the synthesis of biomolecules and other functions. The process of respiration includes both anaerobic (cellular or internal respiration) and aerobic (external respiration). Aerobic respiration requires the presence of molecular oxygen and occurs in mitochondria. Anaerobic respiration does not require the presence of oxygen and is catalyzed by enzymes present in cytoplasm. Both types of respirations have a common series of initial steps termed **glycolysis.**

17.7. METABOLISM

In cell metabolism, big and complex molecules are broken down to simpler molecules by catabolic reactions. At the same time through anabolic reactions smaller molecules are used to synthesis big and complex molecules. Metabolism of differeet constituents of food follow different routes.

17.7.1. Carbohydrate Metabolism

Glucose is the most important of the primary fuels used as a source of energy in living systems. As stated earlier glucose undergoes both catabolic and anabolic reactions (Fig. 17.3). A great deal of energy released in catabolic reactions is efficiently conserved as ATP.

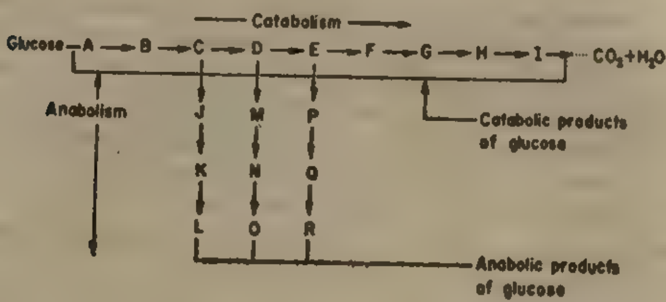


Fig. 17.3. Simplified scheme of catabolism and anabolism of glucose.

The initial phase of glucose utilization is called glycolysis (meaning literally sugar splitting). This takes place in cytoplasm. Glucose is ultimately oxidized to CO_2 and H_2O with the liberation of energy. The first part of the process of many steps consists of anaerobic conversion of the six carbon glucose into two molecules of three carbon units called **pyrivic acid** (Fig. 17.4). It also involves the generation of 2 ATP molecules per molecule of glucose. The various steps involved in the partial oxidation of glucose have been worked on by many investigators. One of these is the **Emden-Meyerhof Pathway** of glycolysis. (Fig. 17.4). Here, bacteria fermentation produces ethanol and in muscles lactic acid is formed.

In the second part of the oxidation unconverted pyruvic acid enters cellular aerobic respiration what is known as the Krebs cycle or Citric acid cycle or Tricarboxylic acid cycle (Fig. 17.5) which is a series of oxidations aided by enzymes that leads to CO_2, H_2O and ATP. This takes places in the mitochondria of cells.

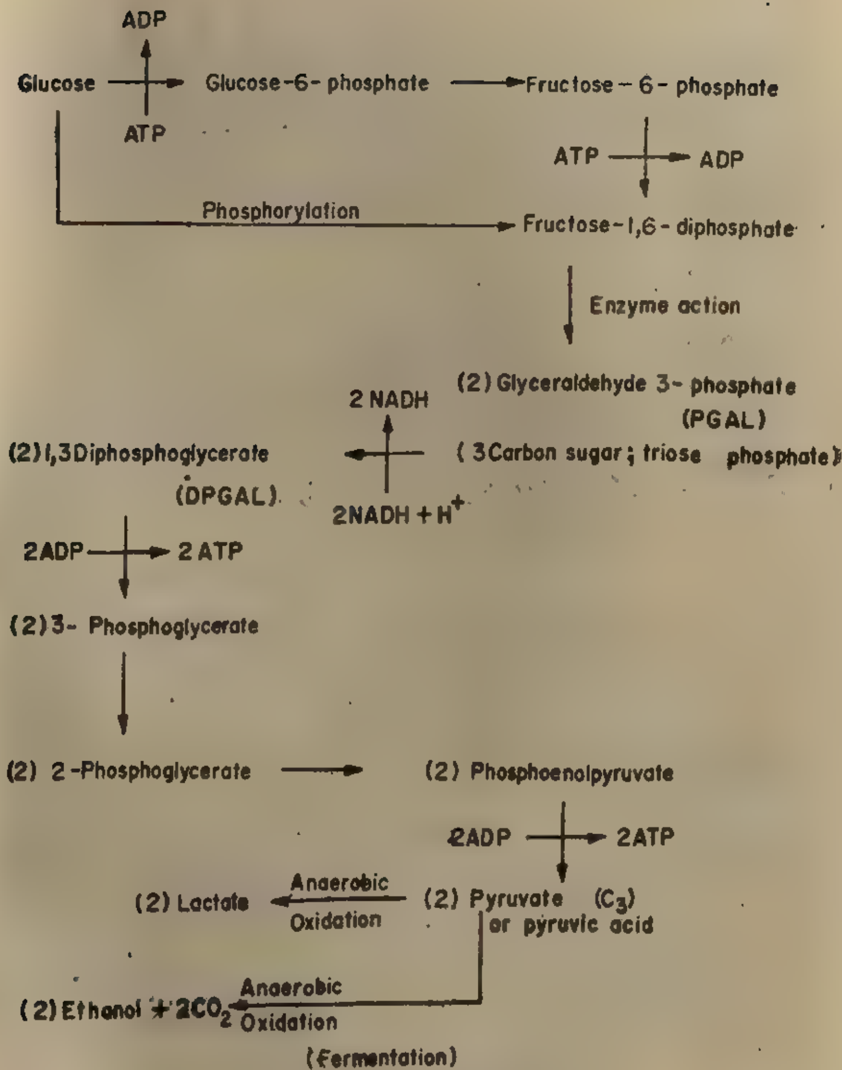


Fig. 17.4. Glycolysis

During aerobic respiration, pyruvic acid in the mitochondria cell, is decarboxylated and the remaining 2-carbon fragment is combined with a molecule of coenzyme A to form "acetyl CoA" followed by the Krebs cycle or Tricarboxylic acid cycle (TCA) and electron transfer.

These processes form both ATP and reduced nucleotides. In the citric acid cycle two molecules of carbon dioxide are formed as

end product. During the oxidation of acetate to CO_2, some coenzyme molecules are reduced. The reduced coenzymes are oxidized (regenerated) via a series of reactions which involve transfer of hydrogen atoms from acetate and other intermediates to oxygen. Such series of oxidation-reduction reactions are known as electron transport chain. Thus electron transport chain produces most of the ATP formed in the oxidation of glucose.

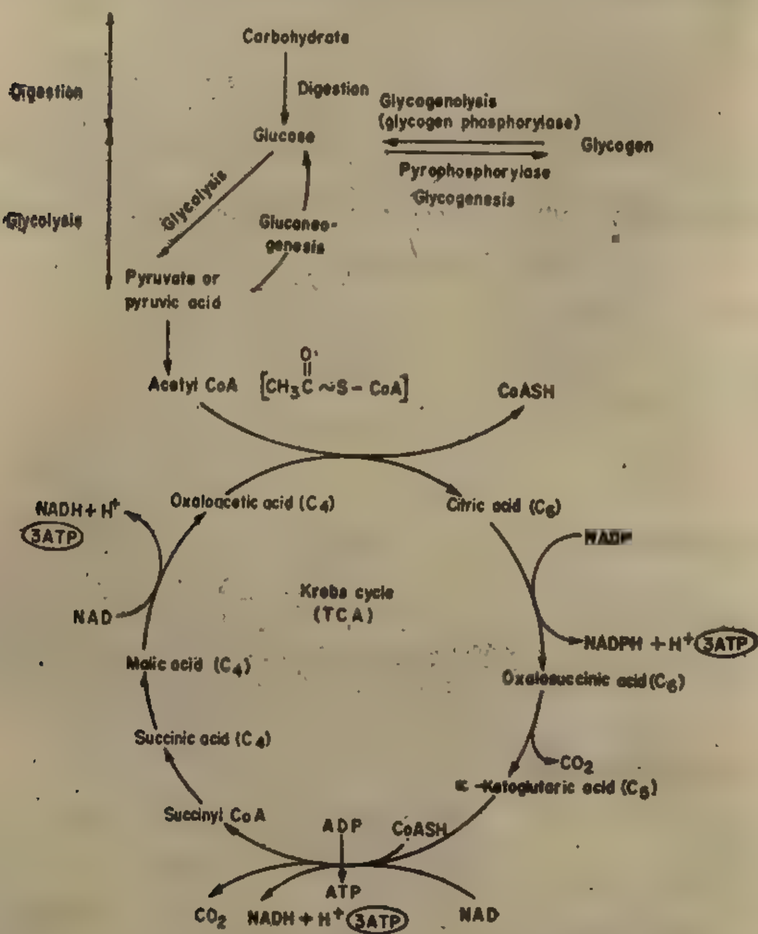


Fig. 17.5. Metabolism of carbohydrate

In glycolysis and the TCA cycle hydrogen is released from different compounds. Oxidation and reduction yield H_2O and energy. In the process energy is trapped rather than totally released as heat. The summary of the reactions is as follows :

$$\text{Glucose} \rightarrow \text{Pyruvic acid} + 4H + 8\ ATP$$
$$\text{Pyruvic acid} + 2CoASH \rightarrow \text{Acetyl CoA} + 2CO_2 + 2H_2 + 6TAP$$
$$\text{Acetyl CoA} + 6H_2O \rightarrow CoASH + 4CO_2 + 8H_2 + 24ATP$$
or,
$$\text{Glucose} + 6O_2 \rightarrow 6CO_2 + 6H_2O + 38\ ATP$$

Thus when one molecule of glucose is broken down, 38 molecules of ATP are produced. Since two molecules of ATP are consumed during the initial step of glycosis, therefore, 36 molecules of ATP are produced on breaking up of each molecule of glucose, *i.e.*, ATP per molecule of glucose is 36.

One mole of glucose (180 g) on conversion into CO_2 and H_2O, releases 2868 kJ energy per mole. This energy is sufficient enough to produce 100 ATP molecules. However, in cells 38 molecules of ATP are produced from one molecule of glucose. This restricts the efficiency of energy conversion to 38 per cent only. This has been found to be greater than any man-made device designed for energy utilization. The remaining 62 per cent of energy is liberated as heat and is used to maintain the body temperature.

17.7.2. Lipid Metabolism

Lipids are stored in body as insoluble triglycerides. Fats are the most calorie-rich food, producing twice as many calories per gram as do carbohydrates. Energy is contained in the long hydrocarbon chains of fatty acids. Enzyme aided hydrolysis and oxidations are the basis of their degradation and bioenergetics. The fat molecule is decomposed to glycerol and fatty acids by the enzyme lipase, Glycerol is converted to glyceraldehyde-3-phosphate, an intermediate product of glycolysis, and join into the glucose metabolism route. This, through series of steps of glocolysis and TCA cycle, yields 20 ATP per molecule of phosphoglyceraldehyde. One molecule of glycerol yields 20+3 ATP of which one ATP is used for phosphorylation so that net gain is 23−1=22 ATP.

The fatty acids are oxidized to CO_2 and water in mitochondria of liver cells and skeletal muscles. To start with it gets linked with CoASH with the energy from ATP. In this process, oxidation occurs at β-carbon atom of a fatty acid followed by cleavage. As a result, two carbon fragments are split off and Acetyl CoA is formed. Acetyl CoA enters TCA cycle and is oxidized to CO_2 and H_2O. For every acetyl CoA 5 ATP are produced.

During complete degradation of palmitic acid, a part of energy is used in producing 130 ATP molecules. This energy is equal to $130 \times 31.4 = 4082\ kJ\ mol^{-1}$ and makes 49% of the available energy. The remaining energy is lost as heat for the body.

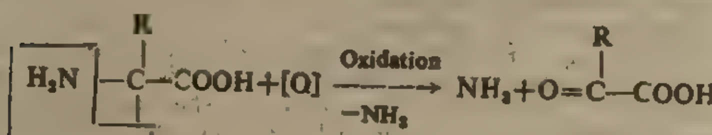
$$\text{Lipids} \xrightarrow{\text{Hydrolysis}} \underset{+\ \text{Glycerol}}{\text{Fatty acids}} \xrightarrow{\text{Oxidation}} \underset{\text{CoA}}{\text{Acetyl}} \xrightarrow[\text{cycle}]{\text{Citric acid}} \text{ATP}$$

17.7.3. Amino Acid Metabolism

Proteins on hydrolysis in the presence of specific enzymes produce amino acids. Amino acids are absorbed into blood from intestine The amino acids have many functions in body. These are the dietary source of nitrogen and find uses in the formation of new cells or repair of old cells, synthesis of other amino acids, enzymes, hormones. antibodies and non-protein molecules such as nucleic acids. Of lesser importance, amino acids serve source of energy (Fig. 17.6). They are not stored in the body like carbohydrates and lipids. Carbohydrates can be stored as glycogen and fats as adipose tissue. Amino acids according to their characteristics are metabolized to pyruvate, acetyl CoA and various intermediates in glucose metabolism (Fig. 17.7). Energy is obtained by breaking amino acids into carbon dioxide and water.

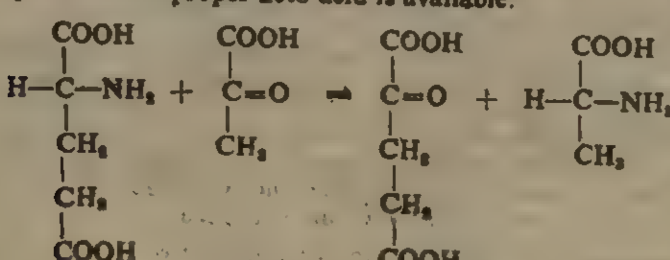
Amino acids enter the respiratory pathways through deamination and transamination.

In deamination, the $—NH_2$ group is removed from the amino acid.



α-keto acid

In transamination, an amino acid is converted into another acid provided the proper keto acid is available.



Pyruvic acid (α-keto acid) | α-ketoglutaric acid | Alanine

The reaction is reversible and provides a means for the conversion of carbohydrates into proteins, as well as the generation of TCA cycle intermediates.

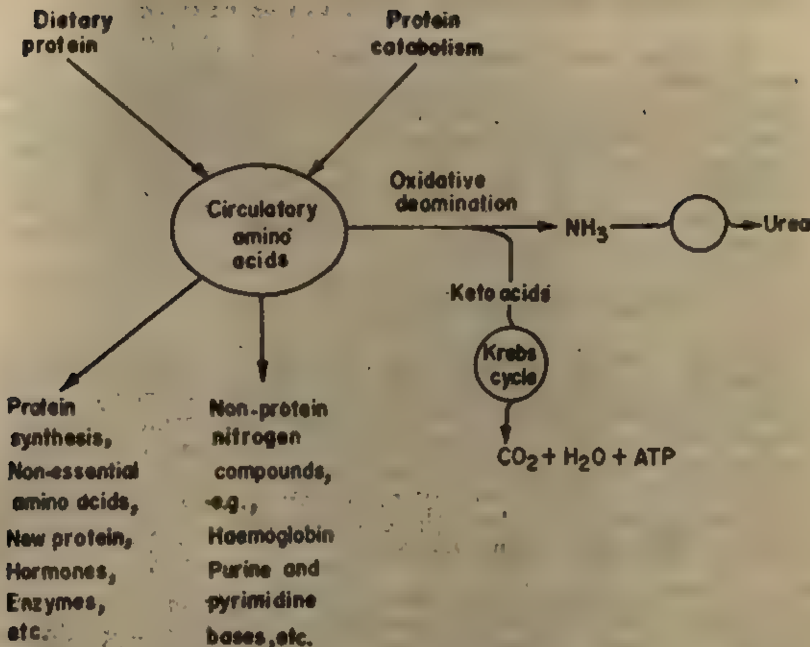


Fig. 17.6. Major uses of amino acids.

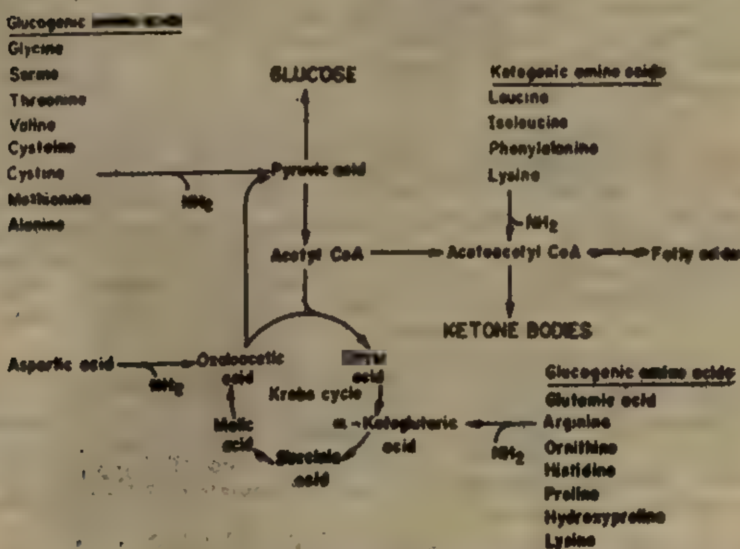


Fig. 17.7. tUilization of amino acids through different routes.

17.8 WATER AND BLOOD : THE VITAL FLUIDS

Various kinds of fluids are present in the human body. Each kind of fluid has its own characteristic composition and functions. All these fluids are vital for life processes. Some fluids are localized at specific sites or regions of the body such as in joints, brains, lungs and heart; while others, *i.e.* water and blood diffuse in the entire organism. The latter class makes almost 70% of the total fluids. The important body fluids are water and blood. All body fluids have water as a common constituent.

17.8.1. Water—The Ideal Physiological Fluid

Water besides being cheap and plentiful is a highly interesting and unique substance from chemical point of view. Water the most abundant liquid in the biosphere, is essential to all forms of life. The characteristic properties of water—remarkable solvent, high boiling point, high heat of vaporization, and abnormally low vapour pressure including the low density of ice are closely related to the structure of water molecule. These properties have staggering influence biologically and environmentally.

The freezing point of water is 273K and its boiling point at 760 mm in 373K. Water is a polar solvent, it is equipped with the property of high dielectric constant and of being able to dissolve many ionic solids. Because of the polar nature of water, plants can acquire the salts which they require for growth by adsorption of these materials into the sap through their roots. Animals absorb substances (polar and ionic materials required for growth) into their blood stream from the aqueous solution in their stomachs and intestines.

Water also dissolves a number of molecular substances, *e.g.*, sugars and alcohols because ot their ability to form hydrogen bonds with water molecules. Without the existence of H-bonds, water would probably be a gas under normal atmospheric conditions; seas, lakes and rivers would never exist and it would never rain. Hydrogen bond also causes higher surface tension and high viscosity. Were it not for this, water would never rise through the capillary tubes in the routes and stems of the plants.

Apart from the properties discussed earlier, water has high specific heat and thermal conductivity. These properties including surface tension are responsible for water to play a vital role in the biosphere. The high heat of vaporization and the high heat capacity of water have a bearing effect on the climate and body temperature of living organisms.

In fact, presence of hydrogen bond in the condensed phase of water is responsible for all the peculiarities and potentialities asso-

ciated with water. We have discussed about water in details in class XI (Unit 12).

Water is the most abundant component of the body. The adult human body contains 60—80 per cent water of its total mass. It is present both in the free and combined states. Almost one half of the body water is bound tightly by cellular proteins, forming the poly electrolyte gel, protoplasm. It is a medium of transport of chemicals across the cell membranes. All metabolic reactions occur in water.

Normally, water distributes rapidly and uniformally throughout the fluid comparments. Water goes to the body through fluid intake, food and as a water of oxidation or metabolic water. Water loss occurs chiefly in the urine. It is also lost via evaporation from the skin and lungs either as insensible or sensible perspiration. Decrease in water content leads to dehydration which at times can be fatal.

17.8.2. Blood

Blood is a red homogeneous liquid and the medium of transport in the circulatory system. Its chemical composition is very complex. It constitutes 0.05 per cent of the total body mass and contains 2.2 per cent solids and about 98 per cent water. In its aqueous solution of salts and certain organic molecules, suspended particles called the red blood cells (erythrocytes), white blood cells (leukocytes) and blood platelets are also dispersed. The pH of the blood is in the range of 7.35—7.62 and its density lies between 1.045 and 1.075.

Blood from which suspended particles are removed is called blood plasma. Blood serum is obtained when fibrinogen a particular protein is removed from plasma. The chief components of the blood and their functions are given in the Table 17.1.

As understood from the Table 17.1, the primary function of blood is transport. The pumping action of heart helps in circulating the blood throughout the body. The blood is the vehicle for metabolic communication between the various systems of the body. It is the medium for transporting nutrients from small intestine to the liver and other organs. It carries with its stream waste products to the kidney for excretion. The blood is also the means for transport of oxygen from the lungs to the tissues. It also transports CO_2 produced in the course of respiratory metabolism of the tissues to lungs for excretion.

The plasma solute concentration in blood is an important factor for proper functioning. This regulates the osmotic pressure of plood plasma and the pH of the blood (Table 17.1).

TABLE 17.1. Chief components of blood and their functions

Components of blood	*Function*
1. Suspended blood particles	
(*a*) red blood cells (RBC)	Help in transporting of molecular oxygen from lungs to tissues.
(*b*) white blood cells (WBC)	Provide defence against infection.
(*c*) blood platelets	Blood clotting.
2. Solutes in plasma	
(*a*) Electrolytes (ions)	
Na^+ and Cl^-	Regulation of osmotic pressure and fluid balance.
HCO_3^-	Acts as buffer in blood. Helps in transporting of CO_2 from cells to the lungs.
(*b*) Proteins	
Albumins	Regulate osmotic pressure of blood plasma, transport of water insoluble substances (lipids).
Fibrinogen	Blood clotting (protective).
Globulins	
alpha, beta	Transport of lipids as lipoproteins.
gamma	Immunological (protective).
(*c*) Carbohydrates	
glucose	Source of energy.

17.8.3. Haemoglobin and Oxygen Transport

Respiration is the process by which gases CO_2 and O_2 interchange between the living organism and environment. The haeme molecule, attached to protein in the blood, is responsible for the transport of oxygen throughout the body (Unit 12). The oxygen molecule becomes reversibly attached to the central iron atoms. The red colour of the oxygen-rich blood (in the arteries) is because of this oxygen-iron complex. Deoxygenated blood (in the vein) is darker and slightly bluish. In lungs, where oxygen is present in higher concentrations, haemoglobin combines with oxygen to form **oxyhaemoglobin**. Here, the oxygen is bound to the iron atom of haeme. In tissues, where oxygen content is low, oxyhaemoglobin dissociates and releases oxygen for utilization. A related protein **myoglobin** serves to store oxygen in the muscle tissues.

The three-dimensional structure of haemoglobin and myoglobin were elucidated by two Cambridge scientists Max Perutz and John

Kendrew respectively (Class XI, Unit 19). They were awarded Nobel prize in 1962 for assigning structures to these compounds. Their structures have helped in understanding the mechanisms of oxygen transport by blood which is one of the vital processes for survival of animals and human beings.

17.9. IMMUNE SYSTEM

The immune system is the body's defence against biological systems that would harm it. The most obvious of these consist of infectious agents, such as viruses or bacteria. The immune system produces immunoglobin, a substance which consists of proteins bound to carbohydrates. This substance works as antibodies against immunogen or antigen macromolecules of polysaccharides, nucleic acids or proteins, characteristic of invasive foreign virus, bacteria or other biological materials. The cells that the immune system uses to provide protection are called leukocytes (white blood cells).

Each lymphocyte produces only one kind of antibody which binds to its surface. This binding, in turn, stimulates rapid division of cells producing daughter cells which are good in production of that antibody. Attachment of an antigen to its at antibody renders the antigen ineffective. Thus, the antigen does not cause any harm to the host. Thus when antigens are administered in response to the entry of antigens or infection the level of the corresponding antibody rises in blood. New born babies do not have a properly developed system for antibody synthesis for several months. During this period, antibodies from mother's milk protect them. It is possible to impart immunity by injecting antigen into another animal such as horse. Now the antibodies are collected from the blood sample of infected animal and are injected in people to protect them from diseases. Immune system has been discussed in details in Class XI (Unit 19).

Foreign agents can cause immune system to over-react with an extreme, self-destructive response called allergy or hypersensitivity. This reaction probably occurs after the foreign materials or their metabolites bind with large molecules endogenous to the body. Among the many substances that cause allergy are pollen, pencillin, pesticides, food additives, resins, plasticizers and certain metals (Be, Ni, Cr).

17.10. HORMONES

Hormones constitute a group of bio-molecules that have an important role in regulating many metabolic processes and sex characteristics. Each hormone usually exerts a specific effect on a certain type of cell or organ to help metabolic processes. They are chemical substances which are secreted by endocrine glands such as

thyriod, adrenals, *etc.* These glands are often called ductless glands because their products, the hormones, are secreted directly into the bloodstream. They are carried by the blood or other fluids to target organs of the body where they exert their influence. Thus they keep sending signals from one cell to another and hence act as messengers Upon receiving a chemical signal, the receptors (chemical entities in target cells) trigger a cell to respond by bringing about specific changes in its properties. A disturbance in hormonal balance may lead to abnormal metabolic processes. They are very potent and hence are produced in small quantities only.

Chemically hormones are quite diverse ranging in structure from proteins to steroids or smaller molecules (amines).

Compounds related to water and salt balance as well as those responsible for characteristics are steroid hormones. Some important hormones with their sources and major functions are given in Table 17.2.

Table 17.2. Hormones and their functions

Hormone	*Source of secretion*	*Function*
1. Steroid hormone		
(*i*) Testosterone (Androgens)	Testis	Responsible for secondary male sex characteristics and development of reproductive organs.
(*ii*) Estrogen	Ovary	Responsible for secondary female characteristics and developement of sex organs.
(*iii*) Progesterone	Ovary	Prepares uterus for pregnancy, affects menstural cycle.
(*iv*) Cortisone, cortico-sterone aldosterone *etc.*	Adrenal cortex	Regulates the metabolism of mineral salts, water, fats, proteins, carbohydrates. Used in the treatment of inflammatory diseases. Excessive secretion increases blood pressure.
2. Peptide hormone		
(*i*) Oxytosin	Pituitary glands	Helps in the contraction of the uterus during child birth and other muscles.
(*ii*) Vasopressin	Pituitary glands	Controls the readsorption of water in the kidneys.
(*iii*) Insulin	Pancreas	Decreases blood glucose level.
(*iv*) Glucagon	Pancreas	Increases blood glucose level.

3. Amine hormone

(*i*) Adrenaline (epinephrine)	Adrenal modulla	Stimulant for sympathetic nervous system ; Increases the pulse rate and blood pressure. Releases glucose from glycogen and fatty acids from fats, fuel for anerobic muscular work.
(*ii*) Thyroxine	Thyroid	Stimulates rate of oxidative metabolism and regulates the general growth and total development Relates to goiter.

Digitoxigenin is another steroid extracted from plant digitalis. It is used as a drug to regulate functioning of heart. It is the raw material for other synthetic steroid drugs.

Androgens and estrogens also have remarkable effects on anabolic system. Athletes, weight-lifters and other sports persons use them to increase the muscle mass and strength. Some female sex hormones which are synthesized on a large scale are used as a oral contraceptives.

A hormone, an octapeptide, Angiotensin II is present in blood plasma of persons with high blood pressure (hypertension) and is a potent vasoconstrictor (constriction of blood vessels).

Inspection of the structures of steroid hormones suggest the presence of steroid nucleus in all with certain differences in substituents. This nucleus is also present in certain vitamins and bile acids. Cholesterol (a steroid alcohol known as sterol) is the starting material for synthesis of all other steroids. Structures of some important steroid hormones have already been given under lipids (Unit 16).

Structures of some peptide hormones

Oxytosin, formed from nine amino acid residues

S–S

Cys–Tyr–Ileu–Gln–Asn–Cys–Pro–Leu–Gly–NH_2

Oxytocin

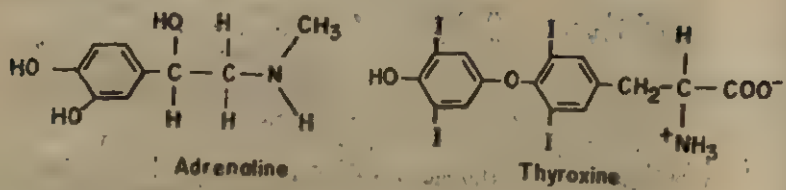
Vapopressin, formed from nine amino acid residues.

S–S

Cys-Tyr-Phe-Gln-Asn-Cys-Pro-Ara-Glv-NH_2

Vasopressin

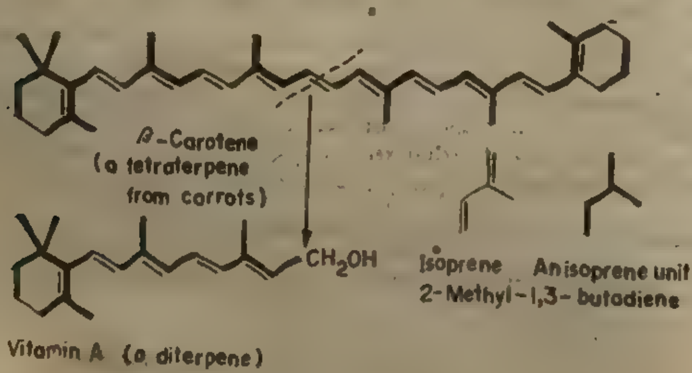
Structures of amine hormones



17.11. VITAMINS

Vitamins are a group of biocatalysts 'vital' for life. They are required by the body in small quantities to maintain normal health and growth. However, these must be supplied through diet or as 'vitamin preparations' as these can not be synthesized by the body. Their deficiency leads to a number of diseases.

1. **Vitamin A** is present in milk, eggs, cod-liver oil and fresh vegetables. It is insoluble in water but soluble in fats and oils. β-carotene, a tetra terpene*, is transformed in the body to vitamin A. The relationship between the structures of β-carotene and vitamin A is shown below. Its deficiency leads to retarded growth, causes diseases like 'xerophthalmia' (in which corners of eyes become opaque), 'xerosis' (in which the skin begins to dry) and 'night-blindness'.



Relationship between β-carotene and vitamin A

2. **Vitamin B-complex** is the name given to a group of water soluble vitamins. Some important ones are :

(*i*) **Vitamin B_1 (thiamine)** occurs in milk, yeast, eggs, rice polishings and vegetables. It is destroyed to some extent on heating. Its deficiency causes loss of appetite and the disease 'beri-beri'.

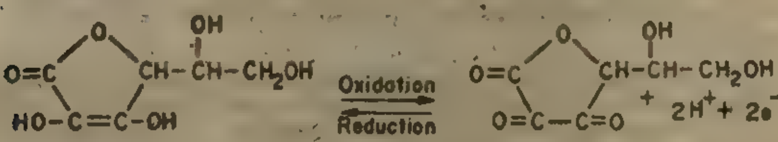
*A terpene is made up of isoprenoid units.

(*ii*) **Vitamin B_2 (riboflavin)** occurs in egg yolk, rice-polishings, milk and vegetables. Its deficiency leads to 'inflammation of the lips', 'sore tongue' and 'skin disorders'.

(*iii*) **Vitamin B_6 (pyridoxine)** occurs in cereals, egg yolk and meat. Prolonged deficiency causes nervous disturbances and convulsions.

(*iv*) **Vitamin B_{12}** is a cobalt containing compound. Lack of this vitamin causes 'anaemia'.

(*v*) **Vitamin C (ascorbic acid)** occurs in citrous fruits (*e.g.*, lemons and oranges), tomatoes, chillies, amla, papita and green vegetables. It is soluble in water and is destroyed on heating and by oxygen in the air even at room temperature. Its deficiency causes 'scurvy'.



Ascorbic acid
(Vitamin C)

Dehydroascorbic acid

4. **Vitamin D** is present in cod-liver oil. It is sometimes called the 'sunshine vitamin', because the ultra-violet radiation of the sun can convert an inactive substance in the skin to vitamin D. It is insoluble in water and soluble in fats and oils. Its deficiency causes 'rickets'.

5. **Vitamin E (tocopherol)** occurs in milk, egg yolk, vegetables and peanut oil. Its deficiency causes 'loss of reproductive ability' and is sometimes called 'antisterility vitamin'.

6. **Vitamin K** is present in leafy vegetables, yeast and egg yolk. It plays an important role in the coagulation of blood.

Vitamins A, D, E and K are insoluble in water and are often called the fat soluble vitamins. Vitamin C and B-complex are water soluble.

The fat soluble vitamins can be stored in the lipids of the body but the water soluble vitamins must be taken daily. If excess of vitamins, especially the fat soluble ones, are taken, then problems of hypervitaminosis (*i.e.*, excessive amounts of vitamins) can occur.

17.12. CHEMISTRY OF SOME DISEASES

Any disturbance in the structure and/or function of an organ or part of the body is called disease. Diseases fall under two major categories : (*i*) communicable and non-communicable diseases.

17.12.1. Communicable Diseases

These are caused by the attack/entry of pathogens (disease germs) into the body and are readily transmitted from one person to another. The infection may also spread through air, water, milk, food, *etc.* Depending upon origin these diseases can be viral, bacterial, protozoal, helminthic and fungal.

I. **Viral Diseases.** Chicken pox, measles and poliomyelitis.

(*i*) **Chicken pox.** It is caused by **varicella-zoster** virus. It starts with mild fever and within 24 hr rashes start appearing on the body. There is no effective treatment. Generally patient is kept in a isolated place.

(*ii*) **Measles.** It is caused by a **myxovirus** and is transmitted by direct contact, *etc.* The common symptoms include fever, dry cough, sneezing, running nose, loss of apetite, *etc.* Vaccines for preventing measles are used to provide resistance against the diseases.

(*iii*) **Poliomyelitis.** It is caused by an **enterovirus.** Its virus enters the body via the alimentary canal where it multiplies and reaches the nervous system through the bloodstream. Contaminated food, water or the faecal-oral route are some of the possible causes. Because of the disease weakness in certain skeletal muscles and their paralysis take place. It is prevented through the use of live or killed polio-vaccines. These days immunizational dose is given in the beginning of infancy.

II. **Bacterial Diseases.** Cholera, typhoid, tuberculosis, leprosy, meningitis, veneral diseases, *etc.*

(*i*) **Cholera.** It is caused by **vibrio cholerae.** Contaminated food and water are the possible source of these bacterias. Flies are the principal carrier of the germs. Its symptom include muscular cramps, vomitting and acute diarrhoea. It is cured by giving glucose, mineral salts, boiled water and antibiotics. These days preventive cholera vaccines are available.

(*iii*) **Typhoid.** It is an infection of intestine and is caused by **salmonella typhi.** Contaminated water, food, *etc.* can cause the disease. The usual symptoms of the disease include continuous fever, slow pulse, diarrhoea, *etc.* It is cured by giving antibiotics. Active immunization with TAB vaccine help in its prevention.

(*iv*) **Tuberculosis.** It is caused by **mycobacterium tuberculosis** which affects lungs, bones, joints, and lymph nodes. The germs are transmitted through discharges during coughing or sneezing or by consuming contaminated food, water, *etc.* Common symptoms of the disease include continuous fever, blood in sputum, cough, pain in chest, loss of body weight, Rifamycin, streptomycin, isoniazed, *etc.* are given to cure the disease. BCG vaccine provides preventive measures.

(*iv*) **Meningitis**. It is caused by **meningococcus**. Its germs usually inhabit the throat, and nasal passages. Its symptoms begin with sore throat, and fever leading to acute headache, stiffness of neck, *etc.* It could be fatal unless immediately attended. In patients suffering from the disease, cerebrospinal fluid becomes turbid.

(*iv*) **Syphilis and Gonorrhoea.** These are veneral diseases. Syphilis is transmitted usually through sexual intercourse with an infected person. Its germs **treponema pallidum** also find its way through cut or crack in the skin. Fever and skin eruptions, *etc.* are the usual symptoms. Gonorrhoea is caused by gonococcus, **neisseria gonorrhoeae**. It is also transmitted through sexual intercourse with an infected person. Infected material may also lead to the disease. Fever, pain, swelling of the joints, and skin eruptions are some of the common symptoms.

III. **Protozoal Diseases**. Malaria, amoebic dysentery.

(*i*) **Malaria.** It is caused by malarial parasite, **plasmodium.** An infected female **anopheles** mosquito when bites a person introduces parasites into the blood stream. Its symptoms include sensation of extreme cold, shivering, severe headace, nausea, *etc.* Quinine is very effective in treating malaria.

17.12.2. Non-communicable Diseases

These diseases result from (*i*) imbalance of essential dietary components of food, *e.g.*, minerals, vitamins, *etc.* (*ii*) general wearing out or degeneration of tissues (*iii*) uncontrolled growth of tissues, (*iv*) defects in the metabolic pathways, and (*v*) injury or damage caused to any part of the body.

Such diseases include coronary heart disease, cancer, diabetes mellitus, *etc.*

(*i*) **Coronary heart disease.** It relates to the insufficient supply of blood to the heart muscles. This is caused by temporary constriction on degenerative changes in the coronary arteries, *e.g.*, thickening and hardening of their walls by fatty material deposition. As a result heart gets inadequate blood and hence to the entire body.

(*ii*) **Cancer.** It relates to the unregulated growth of cells in any parts of the body. Certain cells in a tissue undergo repeated mitotic divisions, *i.e.*, become cancerous and cause its abnormal enlargement termed as tumour. Tumours cells can migrate to the neighbouring tissues through the blood stream and can accumulate at one place leading to secondary tumours. It is believed that gene mutations are responsible for the growth. If diagnosed in the early stages, the disease can be controlled with the help of surgery, radiations and certain drugs. Viral infections, ionizing radiation

and certain carcinogenic agents may cause cancer of lungs, brain, breasts, blood, *etc.*

(*iii*) **Diabetes Mellitus.** It is caused by the lack of insulin in the body. In the absence of insulin, organisms are unable to utilize glucose. As a result, level of glucose in the blood increases. Impaired oxidation of glucose affects metabolism of fats so that the metabolites accumulate in the blood and cause ketosis. This disorder is caused by the defective operation of β-cells of the islands of **Langerhans** in the pancreas which fail to secrete insulin hormone. Its symptoms include rapid weight loss, and frequent urination. Restrictive use of sugar and insulin injection prove helpful in controlling the disease.

In many diseases, the simple treatment is effective because the natural defence of the body can take care of the disease. In some cases, very prolonged treatment is required. Drugs used for treating various diseases will be discussed in Unit 18. You have already studied in details about diseases, nutritional requirements and disorders at Classes X, XI level in your biology classes. More about these, you will study at this level in your biology classes.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

17.1. Choose the correct answer of the four alternatives given for the following questions :

(*i*) The set of reaction in a cell which help in degradation of macromolecules is called

(*a*) catabolism (*b* anabolism
(*c*) metabolism (*d*) all.

(*ii*) The process of respiration in the absence of oxygen is called

(*a*) metabolic (*b*) anaerobic
(*c*) aerobic (*d*) glycolysis.

(*iii*) Which of the following is the end product of protein digestion ?

(*a*) glucose (*b*) glycerol
(*c*) amino acid (*d*) peptide.

(*iv*) One mole of glucose on respiration gives

(*a*) 36 moles of ATP (*b*) 34 moles of ATP
(*c*) 40 moles of ATP (*d*) 38 moles of ATP.

(*v*) A transamination reaction results in

(*a*) urea and keto acid (*b*) amino acid and keto acid
(*c*) amonia and amino acid (*d*) ammonia and keto acid.

(*vi*) Which of the following reactions is in conformity with

$$\Delta G^{\circ} > 50\ kJ\ \text{mol}^{-1}\ ?$$

(*a*) exergonic (*b*) endergonic
(*c*) endothermic (*d*) exothermic.

(*vii*) The hormone that helps in the conversion of glucose to glycogen is
(*a*) cartisone (*b*) gastrine
(*c*) insulin (*d*) adrenaline.

(*viii*) Which of the following macromolecules is not digested by human beings ?
(*a*) maltose (*b*) sucrose
(*c*) amylose (*d*) cellulose

(*ix*) The power house of the cell is
(*a*) cytoplasm (*b*) stomach
(*c*) mitochondria (*d*) intestine.

(*x*) The pH of the fluid in stomach is
(*a*) 2.0 (*b*) 7.0
(*c*) 4.2 (*d*) 9.2.

17.2. Fill in the blanks with appropriate words :

(*i*) ......are the foodstuffs that is used by the body largely for the synthesis of new tissue.

(*ii*) The primary role of carbohydrates in the body is to provide......

(*iii*) Amino acids, called......are not synthesized by the body in adequate quantities.

(*iv*) The......reactions serve to provide both energy for various cellular functions as well as the starting materials for......

(*v*) The process of converting solar energy into chemical energy is called ......

(*vi*) Saliva contains the enzymes......which hydrolyze starch into maltose.

(*vii*) Catabolic reactions proceed with......is free energy.

(*viii*) ......emulsifies fats and allows enzymes to hydrolyse fat into,......and ......

(*ix*) Water serves as medium for transport of chemicals to and from......

(*x*) In lungs oxygen combines with haemoglosin to form......

17.3. Which of the following statements are True (T) or False (F) ?

(*i*) Oxidation of nutrients to CO_2 and H_2O occurs in the process of cellular respiration in mitochondria.

(*ii*) Production of CO_2 occurs in the process known as glycolysis.

(*iii*) The liver converts fructose and galactose to glucose.

(*iv*) Anaerobic oxidation of glucose is called glycolysis.

(*v*) Aerobic oxidation of acetyl CoA is completed *via* the Krebs cycle and respiratory chain.

(*vi*) Total ATP from complete oxidation of glucose including net gain from glycolysis yields in 36 ATP

(*vii*) Insulin is necessary for glucose transport into adipose and muscle tissue.

(*viii*) Proteins are absorbed by the body in their original forms.

(*ix*) Diabetes mellitus is caused by lack of functional insulin.

(*x*) Glucose when enters the cell is trapped as glucose -1-phosphate.

SHORT ANSWER QUESTIONS

17.4. (*i*) How is energy provided to drive an energy-requiring reaction ?

(*ii*) What is meant by the statement that ATP molecules are the currency of energy metabolism in a cell ?

(*iii*) Photosynthesis yields two products that most chemotrophs need to survive. What are they ?

(*iv*) How do yeast cells deprived of oxygen obtain energy from glucose ?

(*v*) What are the products of glycolysis ?

(*vi*) What are the two end-products of cellular respiration ?

TERMINAL QUESTIONS

17.1. Define the following terms :

(*i*) catabolism (*ii*) anabolism
(*iii*) metabolism (*iv*) biomolecules
(*v*) exergonic (*vi*) endergonic.

17.2. How are the biochemical reactions thermodynamically favourable ?

17.3. What are ATP, ADP and AMP ? Why is ATP a store house of energy ?

17.4. Describe the phenomenon of photosynthesis.

17.5. What is digestion ? Describe the digestion of carboydrates, proteins and lipids in details.

17.6. What is cell metabolism ?

17.7. Describe the metabolism of carbohydrates, aminoacids and lipids ?

17.8. What is respiration ? Why is respiration necessary for the living organisms ? How does aerobic respiration differs from anaerobic respiration ?

17.9. Explain the process of glycolysis, and citric acid cycle.

17.10. What are enzymes ? Illustrate their role in various metabolic reactions.

17.11. Explain the following terms :

(*i*) glycolysis (*ii*) cellular respiration
(*iii*) immune system (*iv*) antibodies and antigens.

17·12. Name the vital fluids present in body. What are their composition and functions ?

17.13. What are hormones and vitamins ? What are the biochemical functions of hormones and vitamins ?

17·14. Name the sources and functions of the following hormones in human body ?

(*i*) insulin (*ii*) thyroxine
(*iii*) adernaline (*iv*) cortisone

17.15. What is the cause of diseases in the body ? Describe a few diseases.

ANSWERS TO SELF ASSESSMENT QUESTIONS

17.1. (*i*) (*a*) (*ii*) (*b*) (*iii*) (*c*) (*iv*) (*d*) (*v*) (*b*)
(*vi*) (*b*) (*vii*) (*c*) (*viii*) (*d*) (*ix*) (*c*) (*x*) (*a*)

17.2. (*i*) proteins (*ii*) energy (*iii*) essential amino acids
(*iv*) catabolic, anabolism (*v*) photosynthesis (*vi*) amylases
(*vii*) decrease (*viii*) bile acid, glycerol, fatty acids (*ix*) cells
(*x*) oxyhaemoglobin.

17.3. (*i*) T (*ii*) F (*iii*) T (*iv*) T (*v*) T
(*vi*) F (*vii*) T (*viii*) F (*ix*) T (*x*) F

17.4. (*i*) A basic requirement of various chemical reactions is that they be spontaneous in a thermodynamic sense, *i.e.*, ΔG must be negative. Cells carry out many energy liberating reactions, *e.g.*, carbohydrates and fats combine with oxygen through a series of reactions and finally give CO_2, H_2O and energy.

(*ii*) The P-O-P link present in ATP is the prime source of energy in biological systems. The energy is released when P-O-P link is hydrolyzed to ADP and in true to AMP.

(*iii*) Oxygen and glucose.

(*iv*) Anaerobic respiration (in the absence of O_2) of the stored food takes place

$$C_6H_{12}O_6 \xrightarrow{\text{Enzymes}} 2C_2H_5OH + 2CO_2 + \text{energy}$$

(*v*) Refer to Fig. 17.4.

(*vi*) CO_2 and H_2O.

□ □

UNIT 18

Chemistry in Action

Chemistry ought to be not for chemists alone.

—*MIGUEL DE UNAMUNO (1912)*

UNIT PREVIEW

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Appreciate the impact of chemistry on national economy, and in the welfare of mankind.
2. Distinguish between the natural and synthetic materials.
3. Define dyes.
4. Comment on the classification of dyes.
5. Describe the various chemical reactions involved in the synthesis of dyes.
6. Give the chemical formulae of various dyes.
7. Describe the various chemicals in medicines used as antipyretics, analgesics, antiseptics, disinfectants, tranquilizers and antibiotics.
8. Give the names of natural and man-made fibres.
9. Give the outlines of the process for the preparation, properties and uses of the following :
   (*i*) Acetate rayon, (*ii*) Viscose rayon,
   (*iii*) Cuprammonium rayon, (*iv*) Nylon 66,
   (*v*) Nylon 6, and (*vi*) Terylene.
10. Give the advantages of goods, *e g*, clothes, ropes, etc., made from synthetic fibres over the goods of natural fibres.
11. Give the advantages of synthetic fibre, *e.g.*, nylon and terylene mixed with cotton, wool, *etc.*
12. Distinguish between cotton, wool, silk and man-made fibres.

13. Comment on plant growth hormones and pheromones.
14. Describe the various chemicals and in ceramic industries.
15. Describe the various chemicals used as rocket propellants.

18.1. INTRODUCTION

Chemistry, as we know is the name given to the systematic attempt of describing and explaining the composition of matter and the changes in composition that matter undergoes. Matter, after all, includes everything that is tangible; from our bodies and the stuff of our everyday lives to the most beautiful objects in the universe. Chemistry thus affects every aspect of our lives, our culture and our environment. Its scope includes the air we breathe, the food we eat, the drinks we take, our clothing, our communication and entertainment, transportation, our dwellings, our fuel and energy supplies our life saving drugs, our fellow creatures, *etc.*

All of us are engrossed with the activities of our daily lives that we seldom consider what the world might be like without chemistry. In fact, not a single moment of time goes by in which we are not affected by a chemical matter or a chemical process.

In this unit, we will review a wide variety of natural and man-made substances in which the impact of chemistry is apparent for the well being of mankind.

18.2. DYES

The evolution of the organic chemicals industry started with the discovery of synthetic dyestuffs. Until the 1850's dyes were all produced from living materials, usually plants. Such dyes were found to be limited in colour range and not always technically efficient. **'Mauve'** was the first synthetic dye. It was produced 'just by accident' by W.H. Perkin in 1856. Today, almost all the dyes which are being used, are synthetic dyes. The range of colours and shades available is enormous. Dyestuffs are manufactured on a fairly small scale by relatively lengthy and complex process. Their production thus involve huge expenses. Nevertheless, dyestuffs are essential materials and their high price makes them commercially important.

Azo compounds are the first compounds we have encountered that as a class are strongly coloured. They can be of various colours : orange, red, blue, green depending upon the structure of the molecule. A dye contains a **chromophore group** and a salt

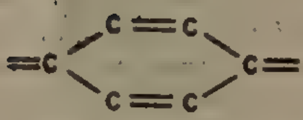
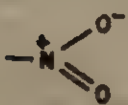
forming group, **anchoric group**. The chromophore group absorbs light of a specific wavelength and reflects back the complementary colour. The specific colour also depends on what other substituents are present; these are called **auxochromes** ($-OH$, $-NH_2$, NR_2, *etc.*). Structurally, dyes do not belong to the same class of compounds. Their mode of use and purpose for which these can be employed differ in many respects. Every dye cannot be employed for all the purposes. A dye which is suitable for cotton fabric may not prove to be suitable for dyeing nylon.

Many of synthetic colouring matter are not considered to be safe for colouring foodstuffs. Hence, their use should be avoided in colouring food stuffs. Only very small number of dyes are considered to be safe to be used for providing colour to food stuffs. Such dyes are known as permitted colours.

18.2.1. Classification of Dyes Based on Their Constitution

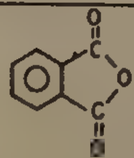
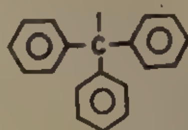
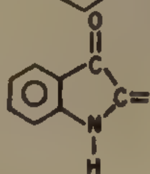
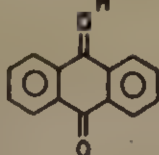
Chemical classification of dyes depends upon the characteristic structural units present in dyes. Some of the common chromophore units present in some common dyes are given in Table 18.1.

TABLE 18.1. Chromophores present in dyes

Chromophore Group	*Name*	*Example*
$-N=N-$	Azo group	Orange-II
$>C=O$	Carbonyl group	
$>C=S$	Thiocarbonyl group	
	Quinoid unit	Rosaniline
	Nitro group	Picric acid
$-\overset{\vert}{C}=\overset{\vert}{C}-\overset{\vert}{C}=\overset{\vert}{C}-$	Conjugated group	

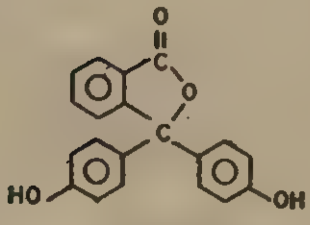
At times dyes are classified on the basis of structural units present in various dyes (Table 18.2).

TABLE 18.2. Some common structural units in some common dyes

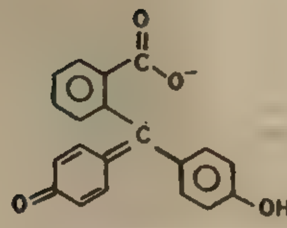
Class of dye	Structural unit	Example
Phthalein		Phenolphthalein
Azo	$-N=N-$	Orange - I
Nitro	$-\overset{+}{N}{\overset{\displaystyle O}{\underset{\displaystyle O^-}{\lessgtr}}}$	Martius yellow
Triphenyl methane		Malachite green
Indigoid		Indigo
Anthraquinone		Alizarin

The chemical formulae of some of the representative dyes are given to give an idea about the variation in their chemical constitutions :

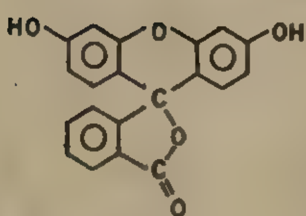
Phthalein dyes



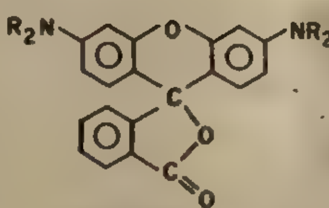
Phenolphthalein
(In acidic medium)



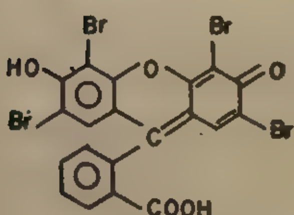
Phenolphthalein
(In alkaline medium)



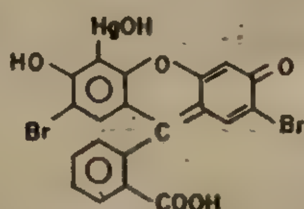
Fluorescein



Rhodamine

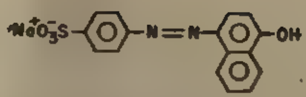


Eosin

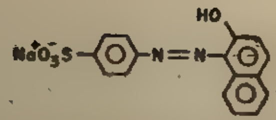


Mercurochrome

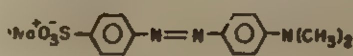
Azo dyes



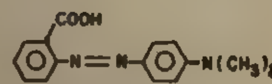
Orang-I



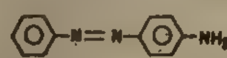
Orange-II



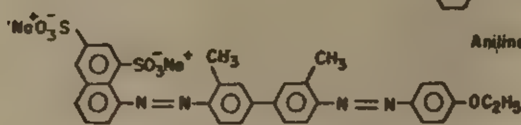
Methyl orange



Methyl red

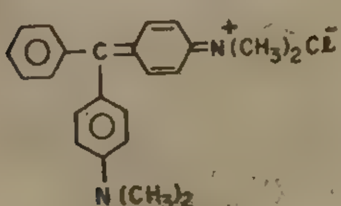


Aniline yellow

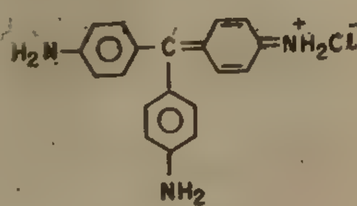


Direct red 39 (bluish red)

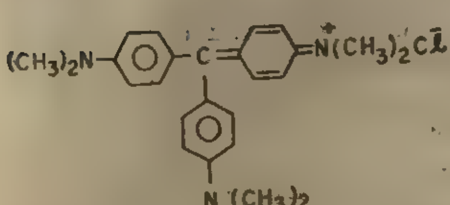
Triphenylmethane dyes



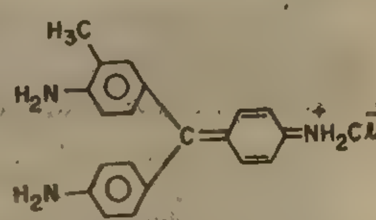
Malachite green



Pararosaniline

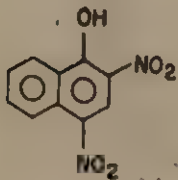


Crystal violet

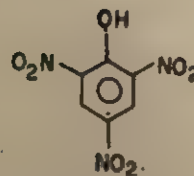


Rosaniline

Nitro dyes

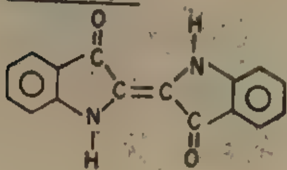


Martius yellow

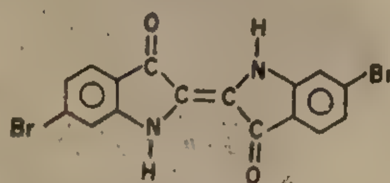


Picric acid

Indigoid dyes

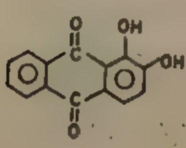


Indigo

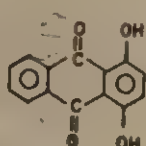


Royal purple
(6,6'- Dibromoindigo)

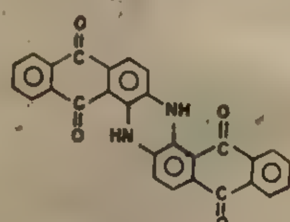
Anthraquinone dyes



Alizarin



Quinizarin



Indanthrene blue I

18.2.2. Classification Based on Application

Dyes require various methods of applying them on various types of materials : cotton, wool, silk, synthetic fibres, papers, leather, *etc.* Thus, dyes may be grouped by the manner in which they can be used. For example, dyes are classified as :

(*i*) Acid dyes
(*ii*) Basic dyes
(*iii*) Direct dyes
(*iv*) Disperse dyes
(*v*) Fibre reactive dyes
(*vi*) Insoluble azo dyes

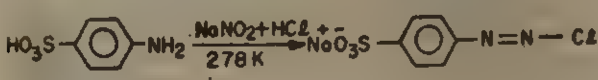
(*vii*) Vat dyes

(*viii*) Mordant dyes

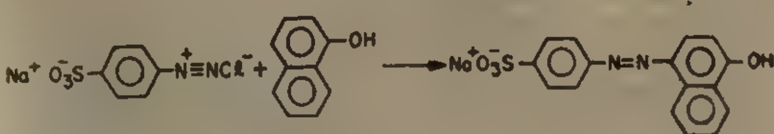
Synthetic dyes are obtained from relatively simple compounds, like benzene, toluene, phenol, naphthol. Coaltar is the rich source of such compounds. These are converted into dye intermediates by reactions such as nitration, sulponation, reduction, oxidation and condensation. Aniline, N, N-dimethylaniline, N-methylaniline, sulphanilic acid, *etc.* are the some of the dye intermediates employed for the commercial preparation of dyes. The dye intermediates are later converted into useful dyes by further suitable chemical reactions.

(*i*) **Acid dyes** : These are the salts of sulphnic acid and nitrophenols. They are used for dyeing wool, silk and nylon fibres. They are not suitable for vegetable fibres, *e.g.* cotton. They are applied to the fibre in a weakly acidic medium. Such dyes normally include nitro aral azo dyes which have sulphonic acid group to make the dye water soluble, *e.g.*, orange I and II.

Orange-I is prepared by coupling of diazotized sulphanilic acid with α-naphthol.



Sulphanilic acid



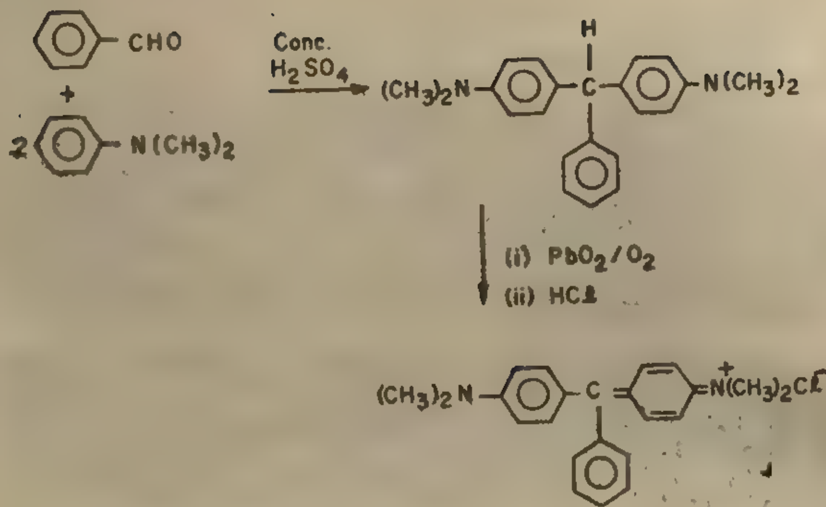
Diazotized sulphanilic acid

α – Naphthol

Orange – I (An acid dye)

(*ii*) **Basic dyes** : Aniline yellow and malachite green belong to this class of dyes. These dyes contain amino acid groups which in acid solution form water soluble cations. These dyes bind themselves through anionic sites present on the fabrics. These dyes are used to dye modified nylons and polyesters.

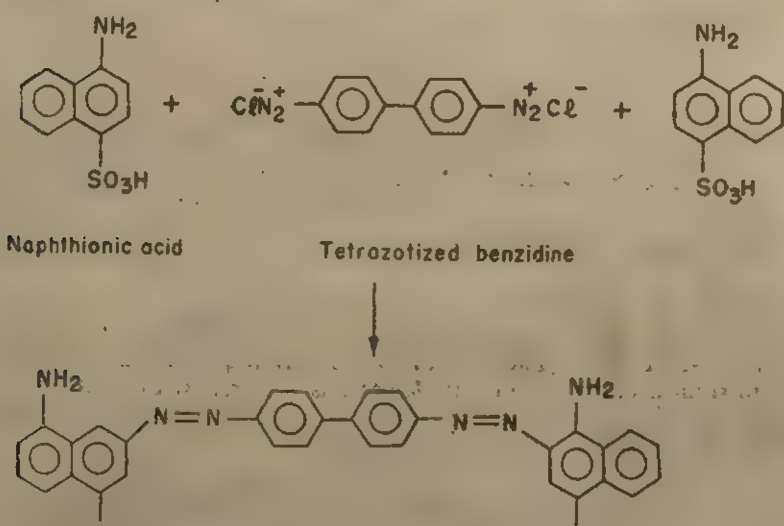
Malachite green is produced by condensing one mole of benzaldehyde with two moles of dimethylaniline followed by oxidation of the condented product (named leuco base ; from Greek word leukas means white) with air (or PbO_2). The oxidized base of the dye on treating the dye with HCl gives the dye cation.



Malachite green

Malachite green is employed for dyeing wool and silk. In case of cotton, tannin is used as mordants along with the dye.

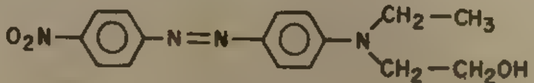
(*iii*) **Direct dyes :** These dyes are directly applied to the fabrics from an aqueous solutions. Thus, these are extensively used for those fabrics which can form hydrogen bonds with dye. They



Congo red

have been found suitable for cotton, rayon, wool, silk and nylon. Martius yellow and congo red fall under this category. Congo red is obtained by coupling tetrazotized benzidine with two molecules of naphthionic acid.

(*iv*) **Disperse dyes :** As the name suggests, the particles of some dyes (present in some dispersing medium) get dispersed in the texture of fabric through diffusion. Such dyes are used for dyeing nylon, polyesters, polyacrylonitrile, cellulose acetate, and certain plastics. Certain azo dyes and authraquinone dyes belong to this class.



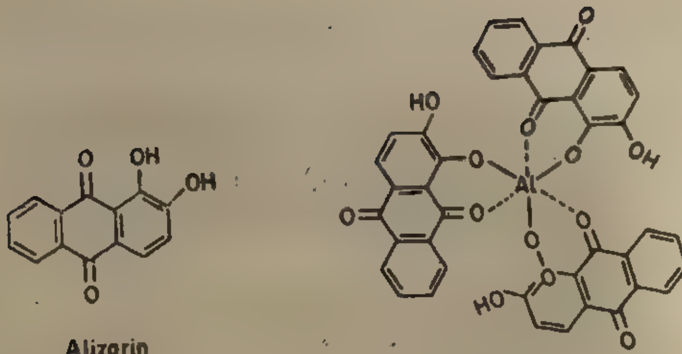
Disperse red I

(*v*) **Fibre reactive dyes :** Dyes of this class form strong chemical bonds with hydroxy or amino group centres on the fibres (cotton, silk or wool) by an irreversible chemical reaction. The colour is fast and last for long.

(*vi*) **Insoluble azo dyes (Ingrain dyes) :** Generally these are synthesized within the fabric during the course of dying process. The cloth is first soaked in an alkaline solution of a phenol (or naphthol) and dried. It is then dipped into a ice cold alkaline solution of a diazonium salt when a coupling reaction takes place. Cotton, silk, polyester and nylon can be dyed by this method. The colour is not very fast as the interaction of the dye and the fabric molecules is only by surface adsorption. Aniline black is a typical dye of this class.

(*vii*) **Vat dyes :** These dyes are insoluble in water. Before applying, dyes are made soluble by reduction method. The soluble form (lecuo) is applied to the fabrics. As a result, the dye is adsorbed on the surface of fibre which, in turn, is oxidized with air or certain chemicals. In the early days reduction process was carried out in wooden vats hence the name 'vat dyes'. These dyes are used to dye mainly cotton. Indigo is a typical example of a vat dye.

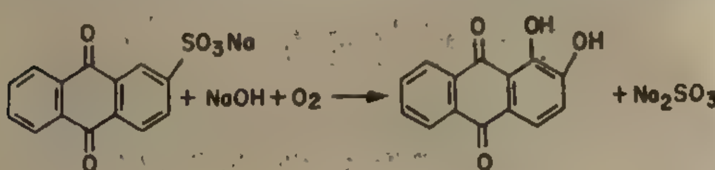
(*viii*) **Mordant dyes :** This class of dyes require a treatment of the fibre with a binding substance or mordant which help in the fixation of dye. The mordant becomes attached to the fibre whch in turn, forms an insoluble complex with the dye. Such a complex is called lake. The commonly used mordants are the oxides of Al, Fe and Cr. The same dye can give different colours depending upon the metal ion used. Alizarin gives a rose red colour with aluminium ion and a blue colour with barium ion. Mordant dyes can be used to dye wool, silk and cotton.



Alizarin

Lake complex

The formation of coloured lakes is the basis of the method of dying by alizarin and other such dyes. Alizanin is produced by the combined action of alkali and an oxidizing agent on anthraquinone -β-sulphonic acid.



Alizarin

18.3. CHEMICALS IN MEDICINES

Perhaps the biggest impact of chemistry on mankind has been in the understanding, prevention and cure of diseases. This has enabled man to live a longer and healthier life. Chemical substances used for treatment of diseases and for reducing the suffering from pain are called medicines or drugs. Chemotherapy is the science in which certain chemicals are employed for the treatment of diseases. This science has grown into vast subject, and efforts are being continuously made to search new drugs for cancer, hypertension, and mental illness among others.

Medicines can be grouped according to the purpose for which these are employed. At times a drug can find use in the treatment of more then one disease.

Before, the extensive use of chemicals as drugs came into existence, early man had used several plants and their products for curing the diseases. The bark of willow tree found its use as an

analgesic. The bark contains, among the other chemicals, derivatives of 2-hydroxybenzoic acid, a breakdown product of aspirin in the body.

The plant Rauwolfia serpentina is used in Ayurvedic system of pathy to treat hypertension (high blood pressure). Reserpine, one of the first drugs used in modern medicine to control hypertension was isolated from the plant just referred. Thus nature paved the way for the development of many new drugs. A large number of other drugs were obtained after careful research.

Chemicals which find their uses in chemotherapy are classified according to their action. Thus, analgesics are those which relieve pain, antipyretics reduce temperature while antiinflammatories reduce inflammation. Antibiotics distroy bacteria and other microorganisms which cause diseases. Some chemicals are used as to supplement the human diet, *e g.*, the vitamins, minerals, *etc.*

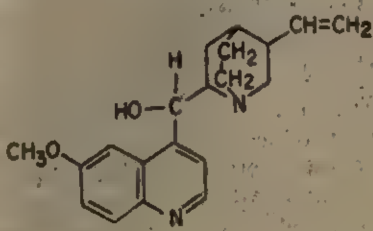
In this section, we will discuss the various chemicals which have been used successfully as drugs.

18.3.1. Chemotherapy

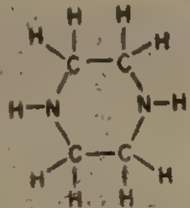
Against many diseases, the natural body defence is supported by chemical substances, either synthetic or isolated from other organisms. Such chemical substances are called chemotherapeutic agents.

Use of drugs for destroying parasitic organisms within a host (patient) is known as **chemotherapy**. Chemotherapy aims at selectively destroying the invading micro-organism without adversely affecting the host. Bacteria, fungi protozoas and viruses are the invading micro-organisms which are responsible for several diseases.

Diseases like pneumonia, tuberculosis, and diphtheria are caused by bacteria. Diseases like malaria, syphilis and dysentery are caused by protozoas. However, viruses (class XI, unit 19 ; high molecular weight non-living proteinous matter which are capable of reproducing when in contact with a suitable host) cause diseases like influenza, smallpox, polio, measles and common cold, *etc.* Several



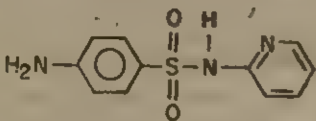
Quinine



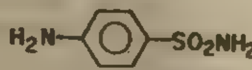
Piperozine

drugs have been synthesized to fight these diseases. For example, quinine and chloroquine are the common drugs used against malaria. Emetine finds use against diseases caused by amoeba. Piperazine is commonly used for destroying round worms and pin worms.

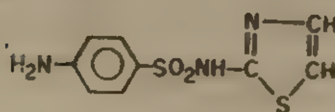
Sulpha drugs like sulphanilamide, sulphathiazole, *etc.* are used for the treatment of throat infection, bronchitis, *etc.* The remarkable



Sulphapyridine



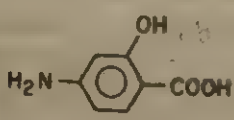
Sulphanilamide



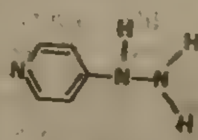
Sulphathiazole

curative power of sulphanilamide was discovered in 1935. Since then compounds similar to sulphanilamide have been developed. They have have been found to be potent germ killers with less toxicity.

Drug like para-aminosalicylic acid (PAS) and iso-nicotinic acid hydrazide or isoniazid (INH) have been found very effective to cure tuberculosis.

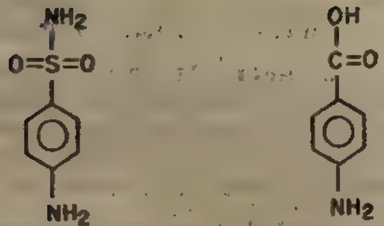


PAS



INH

A theory for the action of chemotherapeutics, is illustrated by the cases of the use of sulphanilamide as a drug. It is believed that sulphanilamide being similar in chemical structure to para-aminobenzoic acid (PABA) can replace the latter in bacteria. However sulphanilamide does not behave as PABA, so that the bacteria is not able to grow or reproduce normally and it eventually dies. Bacteria use PABA for the synthesis of folic acid, which is needed for their existence. It is believed that because of similarity in structure between PABA and sulphanilamide, organisms may



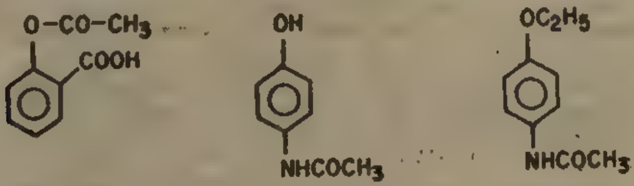
Sulphanilamide PABA

incorporate sulphanilamide and other related compounds into a molecule that is similar to folic acid, but which cannot perform the functions of folic acid. This leads to decreased ability of bacteria to grow and reproduce normally and ultimately to their death.

Chemotherapeutic agents are used singly or in combinations. These should be taken under proper medical care as indiscriminate use can cause damage.

18.3.2. Antipyretics

Antipyretics are drugs which are used extensively to reduce the body temperature in case of high fever. Aspirin (acetyl salicylic acid), paracetamol (4-acetamidophenol), analgin (novalgin) and phenacetin are some of the commonly used antipyretics.



Aspirin Paracetamol Phenacetin

Aspirin is the most popular antipyretic. It gets hydrolyzed in stomach and salicylic acid is produced. Its indiscriminate use over a long period may cause ulcers and bleeding from the stomach wall Therefore, its overdose and prolong use is not advised. However, calcium and sodium salts of aspirin are highly soluble in water and are thus less harmful.

18.3.3. Analgesics

Analgesics are the drugs which are helpful in relieving body pain Aspirin and other antipyretics also act as analgesics.

Analgesics are of two types, *viz.* narcotic and non-narcotic types. Aspirin is the non-narcotic type of analgesics. Thus, aspirin is an antipyretic as well as an analgesics. It does not induce sleep.

Narcotics induce sleep. At time norcotics, when taken in higher doses produce unconsciousness. Alkaloids present in opium, *viz.*, morphine, codeine, heroin are narcotic type. These drugs cause addiction (habit forming), and hence, such medicines should not be used without seeking the advice of a physician.

18.3.4. Antiseptics, Disinfectants and Germicides

Germicides. Chemicals that prevent or even kill micro-organisms are termed germicides.

Antiseptics. These substances kill micro-organisms and can be safely applied on living beings (tissues) such as wounds, cuts, *etc.* They prevent multiplication of germs (Table 18·3).

Disinfectants. Like antiseptics, these kill micro-organisms but their application on living tissues has not been found safe. These are used to sterilize objects like surgical instruments, floors, bathrooms, lavatories, *etc.* (Table 18.3).

Most of the antiseptics and disinfectants are usually poisons (as these interfere with the metabolism of micro-organisms) or powerful oxidizing agents which kill the micro-organisms by their oxidizing action. At times reducing agents like sulphur dioxide, *etc.* are also used.

An antiseptic can also be used as a disinfectant, for example 0.2 per cent solution of phenol can be used as an antiseptic and its 1 per cent solution is used as a disinfectant. Similarly, sulphur dioxide finds use both as a fungioide for sterilization of squashes (for preservation) and as a disinfectant when used in rooms for destroying germs and bacteria.

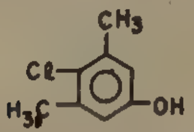
Dyes were amongst the earliest compounds known to be used as antiseptic. Some of them are used even today for the purpose (Table 18.3), *e.g.*, acriflavine (a yellow dye) and mercurochrome (a red coloured compound containing mercury), Gentian violet, methylene blue, *etc.*

TABLE 18.3. Common antiseptics, disinfectants and germicides

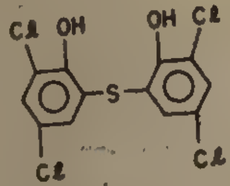
Poison	*Oxidizing agents*
Acriflavine (a yellow dye) Boric acid (mild antiseptic) Bithional	Bleaching powder Chlorine

Chloro-xylenol	
Cresols	
D.D.T.	Hydrogen peroxide
Gention violet	
Formaldehyde	
Hexylresorcinol	
Mercuric chloride	Iodoform
Mercurochrome (a red coloured compound containing mercury)	Iodine
Methylene blue	Potassium permanganate
Phenol	Sodium hypochlorite
Resorcinol	Tincture of iodine
Silver nitrate	

Chlorine water or gas is a popular disinfectant. It is used extensively for sterilizing water. Commonly available antiseptic under the name of Dettol is a mixture of chloro-xylenol and terpeneol in a dispersing solvent. Bithional, a sulphur compound is used in soap industries for manufacturing soaps which can serve as antiseptics.



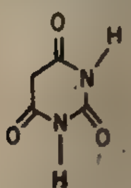
Chloro – xylenol



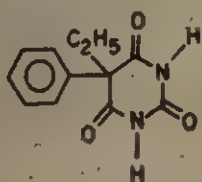
Bithional

18.3.5. Tranquilizers and Hypnotics

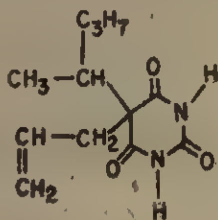
Traquilizers and hypnotics are helpful in reducing anxiety and bring calmness. They act on the central nervous system. Barbituric acid, luminal and seconal are the commonly used tranquilizers. Some are habit forming and their regular use leads to addiction. These are the main constituents of sleeping pills.



Barbituric acid

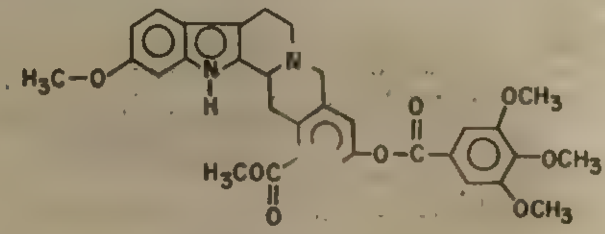


Luminal
(Phenobabital)



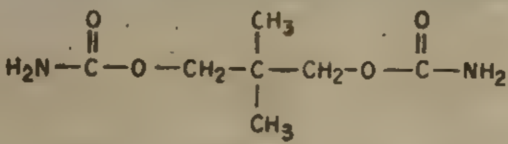
Seconal

Serpasil (reserpine), a drug (alkaloid) obtained from an Indian plant **Raowolfia Serpentina,** is a powerful tranquilizer.



Serpasil (reserpine)

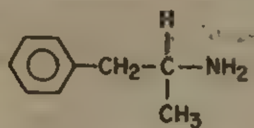
Equanil possesses a good tranquilizing effect and is used in depression and hypertension.

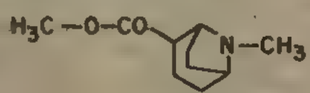


Equanil

18.3.6. Antidepressants

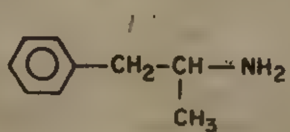
These drugs, when taken, give a feeling of well-being and enhance self confidence by acting on the nervous system. They are known as 'mood boosters'. It is better to use them under medical advice. Tofranil and benzedrine are typical examples of antidepressants. The alkaloid cocaine can also act as mood elevator.





Benzedrine　　　　Cocaine

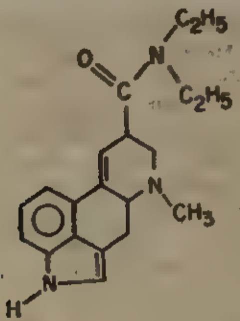
Amphetamines, besides being mild mood-elevators, are also anti-fatigue agents (or stimulants) and are common constituents of 'pep pills' ;



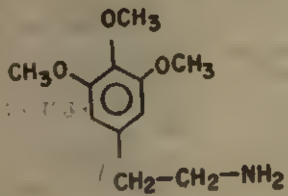
Amphetamine (Parent molecule)

18.3.7. Psychedelic Drugs

Psychedelic drugs are also known as hallucinating drugs These drugs remove anxiety and give a false feeling of happiness. One loses sense of time and space. These drugs disturb vision and hearing. Under the influence of psychedelic drugs a person sees strange colours and hears sounds even though there is none. Lysergic acid diethylamide (LSD) is a powerful psychedelic drug, Mescaline also has similar effects but is less potent than LSD. Such drugs are dangerous and produce ill effects.



LSD



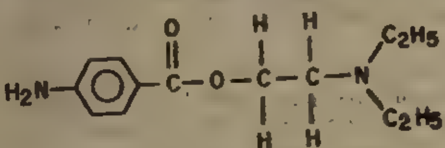
Mescaline

18.3.8. Anaesthetics

Local anaesthetics : These are chemicals which when applied locally produce a loss of sensation in the part. These are used for small surgical operations, like, tooth extraction, or stitching of a small wound. Ethyl chloride and novocaine are common examples.

General anaesthetics : These are chemicals, which when introduced into the body, induce unconsciousness. These are used for major surgical operations. Two examples are cyclopropane and nitrous oxide. Ether and chloroform used previously, have been almost discarded because of the problems associated with their use.

On inhalation of gaseous compounds, these are absorbed through lungs and make a person unconscious, while some others



Procaine

are administered orally or by injections. Morphine and pathedine (which are narcotics) are administered by injection or through oral route.

18.3.9. Antibiotics

Antibiotics are defined as chemical substances produced by micro-organisms (bacteria, fungi and moulds) that can inhibit the growth or even destroy other micro-organisms. They are obtained as the metabolic products of fungi or moulds.

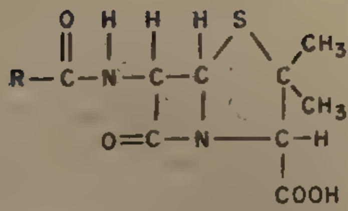
The first antibiotic discovered was penicillin by Alexander Fleming in 1929 from the fungus **Penicillium Notatum**. Although hundreds of antibiotics are known, only a few are useful in treating diseases. A number of antibiotics cannot be used by humans, because although they are toxic to infectious agents they are also toxic for them. It is used against infections caused by various COCCS, **gram positive bacteria**, *etc*. Penicillin is effective against certain infections, *e.g.*, pneumonia, bronchitis, gonorrhea, sore throat, *etc.*, and is one of the 'less toxic' of the common antibiotics. But some individuals have acquired a sensitivity to penicillin so that its use can cause serious consequences for them. Possibly what happens is, that these penicillin sensitive persons produce antibodies to penicillin itself, since penicillin is also a foreign molecule. In this situation, the natural defences of the body (antibody formation) is acting in a way which is not for its own good. This kind of reaction of the body against foreign substances, leads the body to reject new organs put into the body by "organ transplant" operations.

Several modified penicillins are now available. Various other antibiotics like streptomycin (produced by streptomycetes) and tetracycline are used against diseases caused by **gram negative becteria** (*e.g.* infection of the urinary tract). They are also employed in treating infections caused by gram positive becteria which are resistant to penicillin.

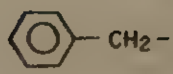
Some antibiotics are very specific as they can help in curing certain diseases, *e.g.*, streptomycin for tuberculosis and chloramphenicol for typhoid. Such antibiotics are included in the category of **narrow spectrum antibiotics**. Penicillin has a narrow spectrum as it is effective against smaller number of micro-organisms.

Antibiotics which can attack a wide range of micro-organisms are called **baoad spectrum** ones. Such medicines are effective against several different types of harmful micro-organism, *e.g.*, tetracycline, chloramphenicol and a mixture of potent antibiotics.

Six natural form of penicillins have been isolated so far.

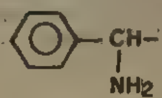


Basic unit of penicillin

R =  Penicillin G or benzyl penicillin

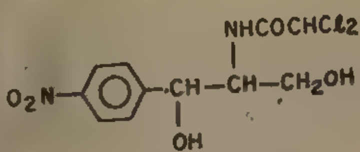
R = $-CH_2-CH=CH-CH_2-CH_3$ Penicillin F

R = $-(CH_2)_6-CH_3$ Penicillin K

R =  Ampicillin

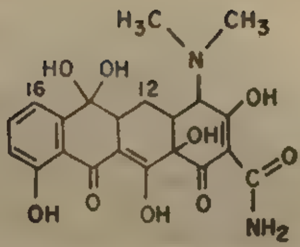
Ampicillin and amoxycillin are the semi-synthetic modifications of penicillin.

Chloramphenicol, a broad spectrum antibiotic was isolated in 1947. It is rapidly absorbed from the gastro-intestinal tract and hence can be given orally in case of typhoid, dysentery, acute fever, certain form of urinary infections, meningitis and pneumonia. It has been proved to be very effective in the treatment of these diseases.



Chloramphenicol

Tetracycline is another antibiotic of proved effectiveness. It 'kills a broad spectrum' of bacteria.



Tetracycline

Aureomycin — - Cl atom at C-16

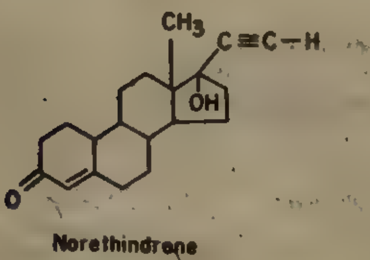
Terramycin — - OH group at C-12

There are many organisms for which both sulpha drugs and penicillin are equally effective; penicillin will act on some for which sulpha is ineffective, and sulpha is useful for treatment in some cases—such as dysentery—in which penicillin seems ineffective. Sulpha drugs are not the metabolic products of fungi or moulds like penicillin. They are all synthetic products.

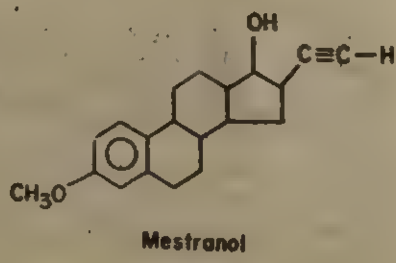
18.3.10. Fertility control

Everyone is concerned about the increasing population. Efforts are being made to control human population. Even chemistry has not lagged behind to offer a solution by providing contraceptive pills.

These usually contain hormones (estrogen and progestin) and which stop ovulation, the movement of an egg down the fallopian tube into the uterus. In the absence of a female egg, pregnancy does not occur. However it is suspected that these have certain undesirable side-effects.



Norethindrone

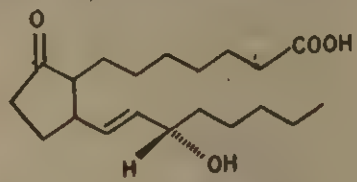


Mestranol

Norethindrone and mestranol are used for making birth control pills.

Recently a group of compounds, called 'prostaglandins', are being tested, for possible use as birth-control drugs.

Prostaglandins are a group of biologically active compounds that are currently receiving a lot of research attention. Chemically they are related to a C_{20} carboxylic acid, eicosanoic acid, that contains a cyclopentane ring. It has been established that unsaturated fatty acids are needed in diet partly for the synthesis of prostaglandins by the body. Prostaglandins have been examined for use in birth control, hypertension, *etc.* It has been suggested that prostaglandins are necessary for normal sexual functions in the male. The most striking feature about prostaglandins is their potency—solutions of as little as 1 nanogram (one billionth of a gramme) per millilitre are able to induce smooth muscle contraction :



'a' Prostaglandin

A possible use of chemicals in medicines for curing various diseases is illustrated through Table 18.4.

18.4. POLYMERS AND FIBRES

We have already discussed about polymers in Unit 15.

Both natural and synthetic fibres are available. Man has used natural fibres for a long time to make clothes and varius domestic articles.

Animals and vegetables are the richest sources of natural fibres. Cotton, flax, jute, *etc.*, are the products of vegetables. Wool, silk, *etc.* are obtained from animals. Vegetable fibres consist of cellulose while animal fibres are made up of proteins.

However, the growing demands of ever increasing population could not be met by natural fibre sources alone. This gave the idea of creating chemical fibres. Artificial fibres are of two types—one is obtained from natural polymers and the other type is obtained from synthesized material. Fig. 18·1 suggests the classification of fibres.

TABLE 18·4. Chemicals in medicine

Chemicals in medicine

- For infectious diseases
  - Germicides (antiseptics, disinfectants), *e.g.*, formaldehyde, phenols, 1% pot. permanganate, mercurochrome
  - Against bacteria
    - Sulpha drugs
    - Antibiotics, *e.g.*, penicillins tetracycline
  - Against parasites, *e.g.*, quinine for malaria
- For treatment of malfunctions of the body
  - Digestion, *e.g.*, castor oil
  - Heart *e.g.*, cardiac glycosides
  - Nervous system and mental state
    - Analgesics, *e.g.*, aspirin
    - Tranquilizer and hypnotics, *e.g.*, reserpine, meprobamate barbiturates
    - Antidepressant iproniazid (marsilid)
    - Stimulant, *e.g.*, amphetamine
    - Psychedelic *e.g.* LSD, mescaline
    - Anaesthetics *e.g.*, tribromomethanol, cyclopropane
- Birth control, *e.g.*, steroid hormones and prostaglandins
- Biological catalysts, *e.g.*, vitamins, hormones

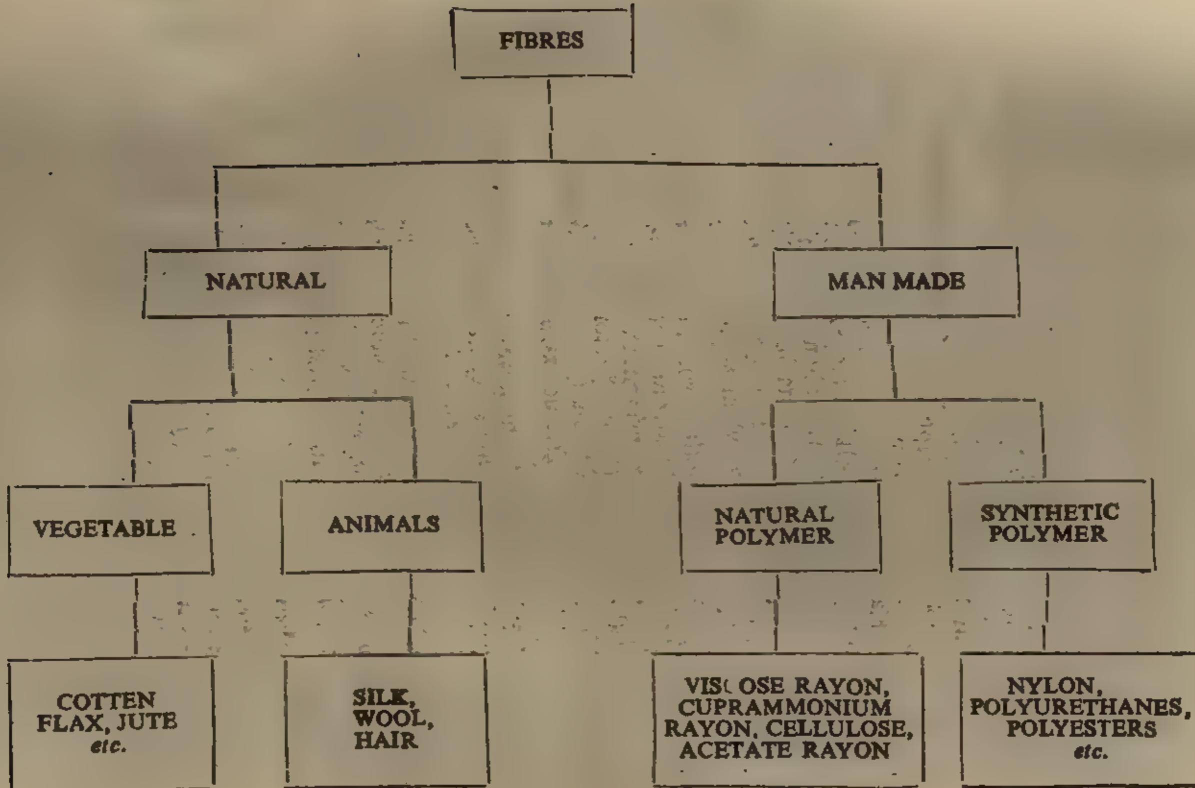


Fig. 18.1. Classification of fibres

18.4.1. Natural Fibres

They are obtained from naturally occurring sources. Based upon the source, natural fibres are of two types : (*i*) vegetable fibres, and (*ii*) animal fibres.

(*i*) **Vegetable fibres**. Plants are the richest sources of vegetable fibres like cotton, jute, *etc*. These are cellulosic products of plant biosynthesis.

(*ii*) **Animal fibres**. They are obtained from animal sources. Wool and silk are the best examples of this class. Wool, a protein, results from animal biosynthesis. It is largely obtained from the hair of sheep. Hair is processed to get wool thread. Silk fibres are obtained from cocoons of silkworms. Silkworms secrete through their glands a viscous solution (or protein solution). In turn, from this solution, they spin a continuous filament of silk which is very thin but very long. Silk thread is obtained by twisting together filments obtained from cocoons of silkworms.

Properties and uses Both cotton and wool fabrics are useful for preparing dresses. Their dresses are very comfortable, and keep us warm in cold weather. They prevent the loss of body heat to the atmosphere because these are bad conductors of heat. When it is hot and humid, the fibres (particularly cotton) in the dress material allow the sweat to go out and give us extra comfort.

Woollen garments do not retain creases. Usually they shrink on ordinary washing. They are susceptible to the attack of moths and mildew.

Cotton garments also shrink on washing. They are attacked by mildew and mould, They readily catch fire The creases ironed into cotton fabrics disappear on washing.

Silk goods are not much in demand as they are very costly.

18.4.2. Man Made Fibres

Naturally occurring fibres like wool, cotton and silk are gradually being replaced by man-made or synthetic fibres which are cheaper and often have better wearing and washing characteristics. Consumers tend to be conservative as the demand is increasing for synthetic fibres that feel and look like natural ones. It is not, therefore, surprising that several synthetic fibres are structurally similar to natural ones.

Man made fibres are of two types : (*a*) regenerated fibres such as rayon (acetate rayon, viscose rayon and cuprammonium rayon), and (*b*) synthetic fibres such as nylon, terylene (dacron), orlon, *etc*.

Regenerated fibres are obtained by processing some natural product, *e.g.*, cellulose, protein, *etc*. Synthetic fibres are primarily

obtained from some synthesized organic products

The raw material is further subjected to mechanical process to convert into filament yarn or staple fibre (*i.e.*, small pieces of filament yarn). To accomplish this, the raw material is either dissolved in some solvent or is taken in a molten form. The solution is passed through small holes called spinnerets of a mechanical spinning device into a coagulating (or solidifying) bath. The temperature and other conditions are so adjusted that filaments formed could get stabilized and retain their shape. During extruding process, the raw material experiences physical or chemical changes.

(*a*) Regenerated fibres

Cotton buds are the starting material for such fibres. It is known as cellulose in the language of chemistry. Now wood-pulp or paper-pulp has taken its place. This pulp (contains cellulose) is dissolved chemically and kept for ageing. During the course of ageing cellulose experiences changes in its physical properties and fibres acquire silky appearance.

Rayons or Artificial silk

Acetate rayon is obtained by the reaction of acetic anhydride on cellulose (wood-pulp, straw, *etc*) in the presence of acetic acid and concentrated H_2SO_4.

$$\underset{\text{(From wood-pulp)}}{[C_6H_7O_2(OH)_3]n} + \underset{\substack{\text{Acetic}\\ \text{anhydride}}}{3n(CH_3CO)_2O} \xrightarrow[\text{Conc. } H_2SO_4]{CH_3COOH} \underset{\substack{\text{Cellulose triacetate}\\ \text{(Tricel)}}}{[C_6H_7O_2(O.COCH_3)_3]n} + 3nCH_3COOH$$

Over a period of 6-8 hr cellulose is completely acetylated at normal temperature.

Cellulose triacetate, a viscous liquid, is mixed with more of glacial acetic acid and dilute H_2SO_4 and allowed to stand overnight at a little higher temperature (say 40°C). Hydrolysis takes place, and acetate is obtained. On further dilution cellulose acetate separates out. Acetone solution of cellulose acetate is passed through capillary size (or small) orifices of a mechanical spinning device along with a current of hot moist air into a coagulating bath. The acetone evaporates and a product called **acetate rayon** is obtained.

To prepare **viscose rayon**, cotton or wood pulp is bleached and treated with concentrated (moderate) caustic soda solution for about one hour followed by carbon disulphide. A deep orange coloured cellulose xanthate is obtained.

$$\underset{\text{Cellulose}}{\text{Cell—OH}} \xrightarrow{\text{NaOH}} \text{Cell ONa}^+ \xrightarrow{CS_2} \underset{\substack{\text{Cellulose xanthate}\\ \text{(Soluble)}}}{\text{Cell—O—}\overset{\overset{\text{S}}{\|}}{\text{C}}\text{—}\overset{-+}{\text{SNa}}}$$

Orange mass, on heating with dilute NaOH goes into solution and a viscous solution called 'Viscose' is obtained. The solution is kept for a week or so for ageing. **Viscose** is extruded under pressure through small orifices of a mechanical spinning device into a coagulating bath containing a mixture of dilute H_2SO_4, sodium sulphate and a small amount of both $ZnSO_4$ and glucose. Xanthate is decomposed here and the regenerated cellulose appears in the form of filaments. This is known as **viscose rayon.**

$$\text{Cell—O—}\overset{\overset{\text{S}}{\|}}{\text{C}}\text{—S}^-\text{Na}^+ \xrightarrow{\text{Acid}} \underset{\text{Viscose rayon}}{\text{Cell—OH}} + CS_2$$

Cuprammonium rayon is obtained as given below briefly: Cellulose is dissolved in an ammonical solution of cupric hydroxide and is separated from suspended impurities. The solution is forced through the orifices of the mechanical device into a coagulating bath containing dilute sodium hydroxide solution. The solution coagulates in the form of fibres. These fibres are treated with dilute H_2SO_4 when cuprammonium complex is decomposed and cellulose is regenerated in the form of filaments having a finer look than those of silk.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

$$Cu(OH)_2 + \text{Liquor } NH_3\ (1:1) \longrightarrow [Cu(NH_3)_4](OH)_2$$

$$\text{Cell—OH} + [Cu(NH_3)_4](OH)_2 \longrightarrow \text{Cellulose solution}$$

$$\Big\downarrow \text{Dilute NaOH solution}$$

$$\underset{\substack{\text{(Regenerated cellulose)}\\ \text{Cuprammonium rayon}}}{\text{Cell—OH}} \xleftarrow{\text{Dil. } H_2SO_4} \text{Coagulated cellulose}$$

The properties of rayon can be improved by, (*i*) slowing down the speed of flow of the raw materials solution (in original or processed form) through the holes in the spinneret, and (*ii*) stretching the newly formed filaments without breaking them.

These treatments increase the tensile strength of rayon fibres considerably.

Uses of Rayon

Some of the major uses of rayon are listed :

1. Lage continuous filaments of rayon fibres are used for tyre cord manufacture.

2. Rayon is used in the manufacture of textiles. Rayon staples are spun and woven into fabrics. Staples can be spun with other fibres such as cotton, wool or linen.

3. Fabric of rayon mixed with cotton in equal ratio is used for making nurses' dresses, aprons and caps.

4. Rayon staple mixed with wool in equal quantities is used in the manufacture of woollen carpets.

5. Rayon thread is used for making lint.

6. Rayon can absorb over 90% of its weight of water. It is superior to cotton and can be obtained in much purer form than cotton. These properties have enabled the use of rayon in the manufacture of gauzes. Further rayon gauzes do not stick to the wounds to the same extent as do the cotton gauzes.

7. Garments of rayon fibre are warmer. They are soft to touch and do not shrink very much after laundry.

8. Fibre of rayon acetate is inferior to cotton with respect to hygiene as it absorbs moisture with great difficulty.

(b) Synthetic fibres

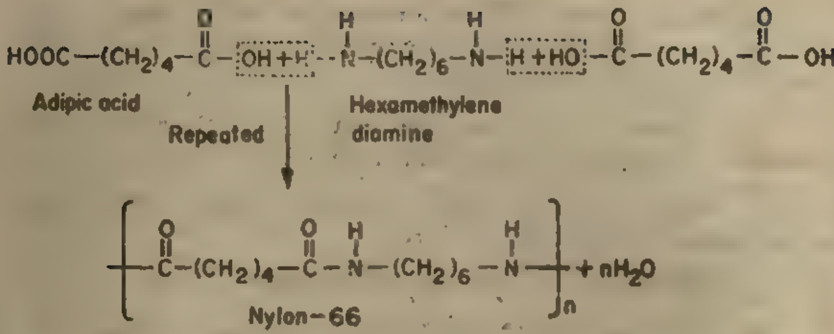
These are the polymerized products. In polymerization, small chemical molecules (monomers) undergo addition or condensation reactions. The resulting molecule is high molecular weight and is known as polymer. These fibres have high tensile strength, resistant to abrasion, resistant to chemical attack and crease resistant. Nylon and terylene are the two most important synthetic fibres.

Nylon

Nylon is the first synthetic fibre which was prepared chemically in 1935 by condensation of small units. The name 'Nylon' is applied to certain long chain polyamides with fibre forming properties. A number of these are known. The two most important ones are called Nylon 66 and Nylon 6.

Nylon 66. It is produced by condensation reaction between hexamethylene diamine and adipic acid, a dicarboxylic acid.

It is so named because it is prepared from starting materials each of which has six carbon atoms.



Repeating unit of Nylon 66

The actual process for the manufacture of nylon 66 employs the 1 : 1 mixture of hexamethylene diamine and adipic acid.

The molten polymer is poured through tiny holes in a spinneret. Emerging from the orifices, the nylon cools to form long filaments which are spun onto spools.

The filaments are stretched to desired length which orients the molecules to strengthen the product.

In addition to fibres, the remolten polymer can be moulded into machine parts such as gears and so on

Properties and uses of Nylon 66

Nylon makes extremely strong threads and fibres because its long chain molecules have stronger intermolecular forces. Fibres are extremely tough, resistant to friction and are chemically inert. The strength of nylon thread makes it suitable for use in making climbing ropes, tufted carpets, strings. fishing nets, parachute fabric, cords, tennis rackets, *etc*. It is also used for making amongst other things, curtain rail fittings, cupboard hinges, machine gear wheels and bearings, hosiery and other clothings, bristles for tooth brushes, surgical sutures, tyre cords and many other things. Water and low temperature do not make the climbing ropes stiff. The ropes are also light, strong and flexible. These properties increase the suitability of nylon fibre for making climbing ropes.

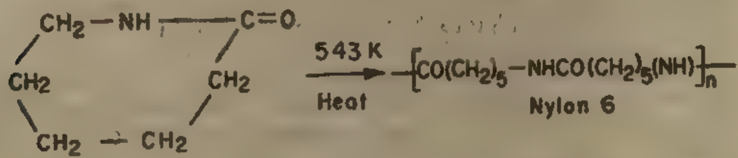
Nylon lacks the softness and moisture absoring properties of the natural fibre. It is, however, harder wearing and has good 'wash and wear characteristics. Nylon clothes become dry rapidly. It is popularly called 'drip-dry' property of nylon.

One of the earliest uses of nylon was as a substitute for silk in the manufacture of ladies stockings. The elasticity, strength, and

dip-dry characteristics of the fibre make it ideal for this purpose. This use was the first major market success for nylon.

Wool is blended with nylon to increase its strength and resistance against abrasion Nylon imparts woollen garments a much longer life. For example, socks made of wool blended nylon (75% wool and 25% nylon) lasts for about five times as long as pure woollen socks. The use of nylon staple with wool (rayon) in manufacturing carpets increases the durability of carpets:

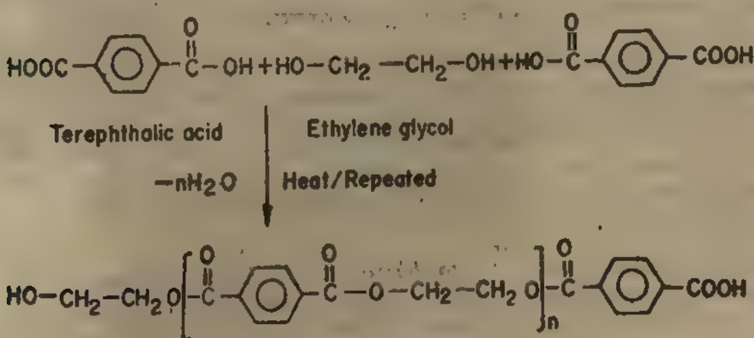
Nylon 6. This polymer is prepared from one type of monomer of six carbon atoms (hence the name Nylon 6), *viz.*, caprolactam.



Nylon is tough and has high tensile strength. It is used as fibre in textile industry, *e.g.*, in elastic hosiery. It is also used for making bristles for brushes, in automobile tyres and many other things.

Terylene

This fibre, also known as 'Dacron' or polyester fibre is made by the condensation of the acid, benzene-1, 4-dicarboxylic acid (terephthalic acid or one of its derivatives, *i.e.*, dimethyl terephthalate) with ethane—1, 2-diol (ethylene glycol) in the presence of a weak base such as calcium acetate.



Terylene or Dacron
(Polyethylene terephthalate)

The polymer is separated and can be melt spun into fibres or processed as a clear film.

Properties and uses of terylene

Terylene is tough, **thermoplastic,** and very resistant to action of chemical or biological substance and to abrasion. It has low moisture absorbing power, and therefore, its clothing dry fast.

Terylene clothes do not get crumped on washings and rough use. Their crease remain intact (crease resistant). This property has enhanced its use in the manufacture of textiles. Further creases set into terylene clothes are fast and long lasting, because of the **heat-setting property**.

Terywool (terylene blended with wool) is widely used for the suiting purposes. Shirts, trousers and other clothes of terycot (terylene blended with cotton) are extremely popular.

Terylene is used for shaping the sails of boats. These sails are light, strong, do not stretch and do not rot in the contact of water. Terylene has proved to be more suitable than nylon for this purpose.

Aprons and other protecting clothings of terylene are used in industries and laboratories. These are resistant to action of chemicals, *etc*.

Terylene has found its use in the hoses used by firemen—as it is tough and quick in drying. Moreover, its hoses do not deteriorate when stored wet.

Further, terylene is used for making magnetic recording tapes because of its high tensile strength.

18.4.3. Identification of Fibres on Burning

(*i*) **Cotton, viscose, rayon and linen** burn quickly to give the odour of burnt paper. They leave grey ash after combustion.

(*ii*) **Wool, silk and man-made fibres** produced from a proteinous natural material burn slowly to give the odour of burnt feathers. Black ball is formed after combustion which can be crushed to powder.

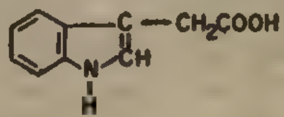
(*iii*) **Nylon and terylene fibres** burn slowly giving an unpleasant odour of burning hair. They soften on heating and then melt and finally form a bead. Fibres can be drawn from their melt.

(*iv*) **Acetate rayon** fibre burns quickly forming a bead (dark brown in colour). Acetate fibre dissolves in acetone (distinction from other fibres).

18.5. PLANT GROWTH HORMONES

Chemical substances which regulate the growth of plants are called plant growth hormones. They are synthesized by plants themselves. There are certain hormones which regulate the regular growth of all the parts, *e.g.*, (*i*) auxins, (*ii*) gibberellines, and gibberellic acids, (*iii*) ethylene, and (*iv*) cytokinin. Apart form these, certain hormones inhibit the process of excessive growth of various parts of plants. They help stemming the multiplication of cells and hence act as growth inhibitors. Abscisic acid is a typical plant growth inhibitor.

Auxins : These plant growth hormones were the first to be recognized. There is another compound, called heteroauxins. Indole-3-acetic acid belongs to the later category of heteroauxins. Auxins assist the process of cell division, root initiation, flower initiation, eradication of weeds, production of fruits and respiration.



Indole-3-acetic acid

Gibberellines and gibberellic acids : These closely related compounds are isolated from parasitic fungus gibberellia fujkuroi found on rice seedlings. They assist in the process of stem elongation, initiation of flowers leaves, fruits, flowers, *etc.*, growth of leaves, flowers and fruits, *etc.*

Cytokinis : These hormones are the degradation products of adenine (a purine base, and component of ATP and nucleic acids). These compounds help the process of cell division, and maintain RNA and purine balance. Through these functions, they keep the leaves of plants in their full gloom. They play a potent role in fruit development, seed germination, *etc.*

Ethylene : The primary function of ethylene is in the post harvest maturation of several fruits like bananas, pears, lemons, tomatoes, *etc.* It also helps in root formation in certain plants, flowering in pine-apple plants, inhibiting sprouting of potatoes. Recognition of ethylene as a potential plant hormone is a recent story.

18.6. PHENOMONES

Visual, accoustical (sound) and contact are some of usual modes of communication seen in human beings. However, among

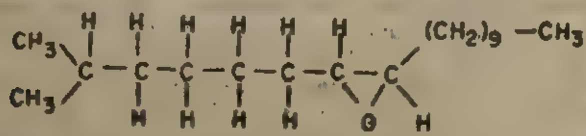
mammal and other simpler animals the usual modes of communication appear to be of chemical nature. Animals generally excrete certain compounds in the environment that influence the behaviour of other animals of the same species. Such compounds are called **pheromones**. These compounds excreted by male/female species serve some other purposes, *e.g.*, to attract members of the opposite sex, to send various types of signals including alarm signals, and to establish contact with organisms of the same species, *etc.*

Pheromones are assuming importance as they have been found useful for insect control. Because of their toxicity over pesticides, they are increasingly being used. They are biodegradable and have to be used in small amounts.

These chemicals have been identified and synthesized. These chemicals are highly specific in their action, as these attract only a particular type of insect. Unlike conventional insecticides these need not be spread over the entire field. The attractant pheromones are placed at one place to which insects are lured and thus collect at one place. These insects then can be killed there.

Looplure, grand-lure and disparlure are some of the well known attractant pheromones. Pheromones have found uses in animal husbandary.

Disparlure has been used to attract gypsy moth.



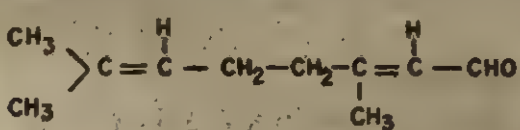
Disparlure

Bombykol, a sex pheromone of female silk worm moth can attract male worms.

$$CH_3-CH_2-CH_2-CH=CH-CH=CH-(CH_2)_8CH_2OH$$

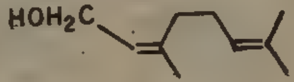
Bombykol

Citral, an alarm pheromone, is excreted by ants when in distress.



Citral

Geraniol, a compound present in roses, is helpful in conveying to honey bees regarding the source of food.



Geraniol

18.7. CERAMICS

Ceramics is the art of producing useful articles entirely or chiefly from raw materials of an earthy nature by high temperature technology. The principal raw material is clay which may be used alone or in combination with other sustances. Building bricks and tile, electrical conduits, electrical and chemical porcelain and stone ware, sanitary ware, artware, domestic ware, porcelain enamels and abrasives, *etc.* are some of the well known ceramic products. Certain ceramic products possessing special mechanical and electrical properties have been developed recently.

Basic raw materials for the ceramic products. Clay, felspar and sand are the three main raw materials for the ceramic products. Clay is mainly impure hydrated aluminium silicate, a weathering product of igneous rocks. Some of the clays include kaolinite ($Al_2O_3.2SiO_2.2H_2O$) montmorillonite [$(MgCa)O.Al_2O_3.5SiO_2.nH_2O$], and illite ($K_2O$, MgO, $Al_2O_3.H_2O$). Clays differ widely in their properties and are accordingly selected and mixed with one another, as well as with other materials, so as to give a composition having the best working properties in the manufacture, consistent with the desired properties of final product. Clays are plastic and mouldable when finely pulverized and wet, rigid when dry and vitreous when subjected to high temperature.

Usual types of felspars used in ceramic industries are : potash K_2O, $Al_2O_3.6SiO_2$; soda Na_2O, Al_2O_3. 6 SiO_2 and lime $CaO.Al_2O_3$. 6 SiO_2.

The other raw materials which find their way in the ceramic industries are :

Fluxing agents. Borax, boric acid, soda ash, sodium nitrate, potassium carbonate, cryolite, fluorspar, apatite, oxides of Fe, Sb and Pb, *etc.*

Refractory materials. Alumina, chromite, aluminium silicates, magnesite, carborundum, dolomite, talc, limestone, *etc.*

Other materials. Various type of silicates, minerals, oxides, certain alkali metals, *etc.*, glazing materials.

Newer Ceramic Products

Ceramic fibres, a variety of textile foam, are used for thermal insulation and high temperatures-low voltage wiring circuits of space and aircraft equipments. Ceramic-reinforced plastic and metal-ceramic laminates are some of the technological materials which can withstand high temperatures.

Barium titanate ($BaTeO_3$), a kind of ceramic product, is used in electrical appliances because of its certain unusual properties. It is ferromagnetic in nature and finds use in television sets, computers, switches, transformeters, *etc.*

Ceramic materials have found their way in the technology of superconducting materials.

18.8. CHEMICALS AS ROCKET PROPELLANTS

It is because of rockets, the historical landing of American astronauts on the moon (July 20, 1969) and the successful space walk by the Russian cosmonauts have been possible. 'Agni', an addition to the list of successful missiles, is also an addition in the successful history of rocket and rocket fuels. India's first settlite launch vehicle, SLV-3, which heralded the coming of age of India's Space Programme also speaks of space rocket technology.

Rockets' upward thrust is based upon the principle of the Newton's Third Law of Motion. Their course of movement is similar to that of a full blown balloon when its air is allowed to escape through a narrow opening. The balloon moves in direction opposite to that of flow of air.

The fire work rockets generally seen on the festive occasions are seen rising high in the sky due to the push of the gases produced by chemical reactions of the explosive materials in them. The space rockets also work almost on the principle of fire work rockets.

Fuels employed in rockets are entirely different from the ones used in automobiles, fire-work rockets, *etc.* An excellent space-rocket fuel must occupy the minimum space and should not add much to the weight of the rocket. If the weight of the rocket is too high, it does not attain the required velocity to go into space.

Moreover, a space rocket passes through regions of no air or very little of it. Thus, an ordinary fuel will not work in the absence of air or oxygen. Hence, a rocket fuel must be such which can provide sufficient oxygen to burn its fuel. Thus, a rocket propellant contains, *viz* fuel and the oxidant.

Propellants, on the basis of their physical states are classified as solid, liquid and hybrid propellants.

Solid propellants. The widely employed solid propellant and known as **composite propellant** is a mixture of a polymeric binder such as polyurethane or polybutadiene as propellant (fuel) and ammonium perchlorate as oxidizer. Other substances like aluminium or magnesium in finely divided state is added to improve the performance of the propellant.

There is another type of solid propellant called **Double base propellant.** It chiefly consists of nitroglycerine and nitrocellulose. Nitrocellulose gels in nitroglycerine sets in as a solid mass. Solid propellant has a distinct property of burning with a pre-determined rate. Once ignited it is not possible to stop ignition or to change the rate of ignition.

Liquid Propellants. Liquid rocket fuels are of mainly two types, *viz.*, **biliquid propellant** and **monopropellants.**

Biliquid propellant is a combination of liquid fuel like kerosene, alcohol, hydrazines, or liquid hydrogen and a liquid oxidizer like liquid oxygen, nitrogen tetraoxide (N_2O_4), nitric acid, *etc.*

TABLE 18.5. Representative combinations of biliquid rocket propellants.

Fuel	*Oxidant*
Liquid hydrogen	Liquid oxygen
Kerosene oil	Liquid oxygen
Hydrazine ($H_2N.NH_2$)	Nitric acid

(Table 18.5). The biliquid propellants, in general, give higher upward thrusts than solid propellants. The thrust can be controlled by regulating the flow of the propellant.

Monopropellants are liquid propellants which contain only one chemical compound. On decomposition or ignition, it emits a large volume of hot gases. Liquids like hydrazine, methyl nitrate, nitromethane and hydrogen peroxide belong to this type of propellants. Besides hydrazine the other liquid compounds just listed can work both as fuel and oxidizer.

Hybrid rocket propellants. As the name suggests these are a combination of a solid fuel and a liquid oxidizer, *e.g.*, a mixture of acrylic rubber and liquid N_2O_4.

The energy of a propellant is measured in terms of its specific impulse (I_s). The specific impulse of a propellant is given by the relationship.

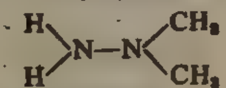
$$\boxed{I_s = \sqrt{\frac{T_c}{M}}}$$

where T_c = flame temperature inside the rocket motor.
M = average molecular mass of the hot gases.

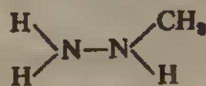
Accordingly a propellant like H_2F_2, with a high exothermicity and low molecular mass of the hot gases (products) will be an ideal propellant from energy consideration. However, safety in handling and overall cost of production are some of the important factors which are taken into consideration for employing a propellant system.

Space programmes and fuels

In India's SLV-3 and ASLV rockets, composite solid propellants were used. The PSLV-rocket, which is still in the experimental stage, will employ a solid propellant in the first and third stages while its second stage will use liquid propellants consisting of N_2O_4 as oxidizer and unsymmetrical dimethylhydrazine (UDMH). For the fourth stage the proposed propellant is a combination of N_2O_4 and monomethylhydrazine (MMH).



UDMH
Unsymmetrical dimethylhydrazine



MMH
Monomethylhydrazine

PSLV Test Successful

NAGERCOIL, March 23, 1990 (UNI) : A milestone in the development of the Polar Satellite Launch Vehicle (PSLV) has been crossed with the successful ground test of its second-stage liquid propulsion "Vikas" engine at Mahendragiri, near here.

The full duration test of the battleship stage of the giant PSLV was carried out on Wednesday at the Liquid Propulsion Systems Centre.

The Titan **ballistic missile** uses hydrazine as a fuel and nitrogen tetroxide (N_2O_4) as oxidizer. The space shuttle uses a mixture of liquid hydrogen and oxygen coupled with solid boosters in the lower stages of rockets.

The **Saturn booster rocket** (used in the American Space Programme) derives its thrust energy from biliquid propellants. In the initial stage a combination of kerosene and liquid oxygen is used and in the upper stages a combination liquid oxygen and liquid hydrogen.

The Russian rockets such as **proton** generally used a biliquid propellant, a combination of kerosene and liquid oxygen.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

18.1 Choose the correct answer of the four alternatives given for the following questions :

(*i*) Which of the following dyes has a azo group ?

(*a*) Rhodamine (*b*) Methyl red
(*c*) Malachite green (*d*) Crystal violet

(*ii*) Which of the following dyes has been classified as direct dye ?

(*a*) Congo red (*b*) Martius yellow
(*c*) Alizarin (*d*) Malachite green

(*iii*) Which of the following metal ions imparts a red colour in combination with mordant dye ?

(*a*) Cu^{2+} (*b*) Cr^{3+}
(*c*) Al^{3+} (*d*) Fe^{3+}

(*iv*) Which of the followings drugs is used as antipyretic ?

(*a*) Equanil (*b*) Sulphadiazine
(*c*) Luminal (*d*) Aspirin

(*v*) Which of the following drugs is used for lowering blood pressure ?

(*a*) Reserpine (*b*) Cocaine
(*c*) Paracetamol (*d*) Chloramphenicol

(*vi*) The raw material for making Nylon 6 is :

(*a*) Caprolactam (*b*) Butadiene
(*c*) Adipic acid (*d*) Phthalic acid

(*vii*) Nylon 66 is a co-polymer of

(*a*) Phenol and formaldehyde
(*b*) Phthalic acid and ethyleneglycol
(*c*) Phthalic acid and ethyl alcohol
(*d*) Adipic acid and hexamethylene diamine

(*viii*) A combination of nitrocellulose and nitroglycerine is a propellant of the type

(*a*) hybrid propellant (*b*) monopropellant
(*c*) double base propellant (*d*) biliquid propellant

(*ix*) Which of the following propellants was employed in SLV-3 ?

(*a*) composite solid propellant

(b) biliquid propellant
(c) UDMH+liquid N_2O_4
(d) MMH+liquid N_2O_4

(x) Which of the following is a general anaesthetics ?
(a) Xylocaine (b) procaine
(c) cocaine (d) nitrous oxide

18.2. Fill in the blanks with appropriate words :

(i) Malachite green belongs to the class of.........dyes.

(ii) Azo dyes are obtained by coupling of a.........with a diazonium salt.

(iii) Tranquilizers, called.........drugs are the constituents of sleeping pills and are used for the treatment of.........

(iv) Methylene blue is employed as an.........

(v) Chloramphenicol is a.........antibiotic and is used to treat......*etc.*

(vi) Pheromones, the compounds excreted by animals/insects, influence the behaviour of other animals/insects of the.........

(vii) Cytokins, the plant growth hormones, are the degradation products of.........

(viii) The artificial silk prepared from cellulose is called.........

(ix) A mixture of liquid hydrazine and liquid oxygen is employed as a.........

(x) A dye essentially has an.........group.

18.3. Which of the following statements are true (T) and false (F) :

(i) Indigo is one of the earliest known natural dyes.

(ii) Congo red, an azo dye, is a typical example of vat dyes.

(iii) An antipyretic is a substance that relieves pain.

(iv) Equanil is used for patients suffering from depression and hypertension.

(v) Tetracycline is a broad spectrum antibiotic.

(vi) Cotton, viscose and linen burn but not vigorously and give smell of burning feathers.

(vii) Acid dyes are applied in aqueous acidic solution.

(viii) A monopropellant works both as a fuel and oxidizing agent.

(ix) Sulphadiazine is an antibiotic.

(x) Phenol is used both as an antiseptic and disinfectant.

TERMINAL QUESTIONS

18.1. What are dyes ? List the basic properties which a compound must possess to be used as a dye for fabrics.

18.2. Give one example with chemical formula for the following class of dyes :

(i) azo dye

(*ii*) triphenylmethane dye
(*iii*) nitro dye
(*iv*) phthalein dye.

18.3. What are synthetic dyes ? Suggest the name and structure of one synthetic dye from each class given in question 18.2.

18.4. Classify the following dyes according to the structural unit present in them :

(*a*) indigo
(*b*) alizarin
(*c*) malachite green
(*d*) phenolphthalein
(*e*) orange-I,
(*f*) congo red
(*g*) martius yellow.
(*h*) picric acid.

18.5. Give classification of dyes based upon their method of application.

18.6. What is chemotherapy ?

18.7. What are drugs ? Suggest a few important drugs about which you have heard with their applications.

18.8. Explain the following terms and give at least one example for each of them.

(*a*) Antipyretic
(*b*) Analgesics
(*c*) Antiseptic
(*d*) Disinfactant
(*e*) General anaesthetics
(*f*) Tranquilizer
(*g*) Local anaesthetics
(*h*) Antimalarial
(*i*) Antibiotic
(*j*) Sulpha drug.

18.9. What are modified penicillins ? How do they differ from penicillin ?

18.10. What are broad spectrum antib iotics ? Give two examples. In what ways they are more useful ?

18.11. What are tranquilizers and hypnotics ? Give one example of each type. Do they cause any side effects ?

18.12. What is the difference between an antiseptic and disinfectant ?

18.13. Give some of the uses of the following :

(*i*) Aspirin
(*ii*) LSD
(*iii*) Morphine
(*iv*) Cocaine
(*v*) Streptomycin
(*vi*) Mestranol.

18.14. Suggest a few chemicals that can help in the control of fertility ?

18.15. What is the difference between local and general anaesthetics ?

18.16. Give reasons briefly for the following :

(*i*) Cotton and woollen dresses keep us warm in winter.
(*ii*) Cotton clothes keep us comfortable in hot weather.
(*iii*) Nylon is a suitable material for making climbing ropes.
(*iv*) Nylon has a dip-dry property.
(*v*) Wool is blended with nylon.

18.17. Why are cotton clothes being replaced by synthetic fibre clothes ?

18.18. Name three important rayons with their characteristics.

18.19. Give the characteristics of nylon fibres.

18.20. (*a*) Name two natural fibres and two man-made fibres.

(*b*) Mention importnnt uses of rayon fibres.

(*c*) What are the raw materials used for making rayons ?

18.21. List important properties and uses of nylon and terylene.

18.22. How will you distinguish between cotton, wool, silk and artificial fibres ?

18.23. What are pheromones ? How are they classified ? How do these compounds help the animals/insects ?

18.24. What are plant growth hormones. Suggest their uses.

18.25. (*a*) Name the principle on which a rocket is able to move ?

(*b*) Are the propellants used in space rockets are different from ordinary fuels ?

18.26. Give an example of solid propellant ? Name the propellant employed in SLV-3.

18.27. (*a*) What are biliquid propellants ? Give two examples of this class of propellant.

(*b*) What is a monopropellant ? Give one example of such a propellant.

18.28. Explain the terms :

(*i*) Propellant (*ii*) Hybrid propellant

(*iii*) Fuel (*iv*) Double base propellant

18.29. (*a*) What are ceramics and ceramic products ?

(*b*) What are the basic constituents used in ceramic industries ?

18.30. Give a brief account of the importance of chemistry in our daily life.

ANSWERS TO SELF ASSESSMENT QUESTIONS

18.1. (*i*) (*b*) (*ii*) (*a*) (*iii*) (*c*) (*iv*) (*d*) (*v*) (*a*)
(*vi*) (*a*) (*vii*) (*d*) (*viii*) (*c*) (*ix*) (*a*) (*x*) (*d*)

18.2. (*i*) basic (*ii*) phenol or naphthol
(*iii*) psychotherapeutic, mental diseases,
(*iv*) antiseptic (*v*) broad spectrum, typhoid, pneumonia
(*vi*) same species. (*vii*) adenine.
(*viii*) rayon (*ix*) propellant
(*x*) chromophore.

18.3. (*i*) T (*ii*) F (*iii*) F (*iv*) T (*v*) F
(*vi*) F (*vii*) T (*viii*) T. (*ix*) F (*x*) T

□□

EXAMINATION PAPERS—CHEMISTRY 1990

Central Board of Secondary Education, New Delhi

(Note : These papers were found at various Centres in Delhi and outside Delhi. These are based on the Syllabus which was introduced in Kendriya Vidyalyas in XII Class in 1989 for which they were examined in 1990. From 1991 examination, all schools under CBSE will follow this syllabus.)

PAPER I

Time allowed : 3 hours *Maximum marks : 70*

Note : *Attempt all questions.*

1. (*a*) Why is bond order in H_2^- less than that in H_2 ?

(*b*) Which point defect may lower the density of an ionic crystal ?

(*c*) Why is NCl_5 not formed ?

(*d*) What is the main use of the following nuclear disintegration ?

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

(*e*) What is cathodic protection of iron ?

(*f*) Why is ionic radius of Cu^{2+} less than that of Cr^{2+} whereas atomic number of Cu is greater than that of Cr ?

(*g*) Write all the isomers of $[Co(NH_3)_5\ SCN]\ Cl_2$.

(*h*) What are the two functions of nucleic acids ?

(*i*) What type of drug chloramphenicol is ?

(*j*) What are Vat dyes ? 1×10

2. (*a*) When would the wavelength associated with an electron be equal to the wavelength associated with a proton ? (mass of electron$=9{\cdot}1095 \times 10^{-28}$ g, mass of proton $=1{\cdot}6725 \times 10^{-24}$ g)

(*b*) An element 'A' (atomic mass 100) having b.c.c. structure has unit cell edge 400 pm. Calculate the density of A and the number of unit cells for 10 g of A. (Avogadro number$=6{\cdot}023 \times 10^{23}$).

(*c*) The reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}\ O_2$ is of first order in N_2O_5. Its rate constant is $6{\cdot}2 \times 10^{-6}\ s^{-1}$. If in the

beginning $[N_2O_5]$ is 15 mol L^{-1}, calculate the rate of reaction in the beginning.

(*d*) What is energy of activation ? How is the rate constant of a reaction related to its activation energy ? 2×4

3. (*a*) Heat of combustion of CH_4 (g) at constant volume and at 298 K has been found to be —885k J/mol. Calculate the enthalpy of its combustion under constant pressure condition (R=8·31 J mol^{-1} K^{-1}).

(*b*) Calculate the energy released in the nuclear fusion reaction : ${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n$. Atomic masses are :

${}^{2}_{1}H = 2·014$, ${}^{3}_{1}H = 3·016$, ${}^{4}_{2}He = 4.003$, ${}^{1}_{0}n = 1·009$ (all in amu).

(*c*) Explain the terms 'Brownian movement' and 'peptization'.

(*d*) Explain the geometry of Ni $(CO)_4$ by valence bond theory. Why is this molecule diamagnetic ? (Atomic no. of Ni=28). 2×4

4. (*a*) How will you convert (*i*) ethanol to ethylene. (*ii*) acetone to 2-methyl-2-propanol ?

(*b*) How will you distinguish benzaldehyde from (*i*) acetaldehyde (*ii*) acetone ? Give reactions.

(*c*) Write IUPAC name of phenyl cyanide. How will you convert aniline into phenyl cyanide ?

(*d*) Explain the 'chain growth polymerization' and 'step growth polymerization'. 2×4

5 (*a*) Explain the terms 'multimolecular colloids' and 'macromolecular colloids'.

(*b*) Explain the following :

(*i*) Cu^+ is colourless whereas Cu^{2+} is blue in aqueous solutions [at. no. of Cu=29].

(*ii*) O_2 is paramagnetic whereas N_2 is diamagnetic.

(*c*) Explain the functions of triglycerides and phospholipids.

(*d*) Explain the light and dark reactions of photosynthesis. 2×4

6 (*a*) How is n-propyl alcohol obtained from ethylene ? How will you convert this alcohol into propylene and n-hexane?

(*b*) How will you synthesize salicylic acid from phenol ?

(*c*) What happens when :

(*i*) an alkyl halide is reacted with AgCN and the product hydrolyzed,

(*ii*) aniline is diazotized and the product reacted with phenol,

(*iii*) methylamine reacts with chloroform and KOH. 3×3

7. (*a*) Explain the terms entropy and enthalpy.
ΔH and ΔS for $Br_2(l) + Cl_2(g) \rightarrow 2\,BrCl(g)$ are 29·37 kJ mol^{-1} and 104·0 J.K^{-1} mol^{-1} respectively. Above what temperature, will this reaction become spontaneous ?

(*b*) Calculate the E.M.F. of the cell Mg (s) | Mg^{2+} (0.2 M) || Ag^+ (1×10^{-3} M) | Ag $E^\circ_{Ag^+/Ag} = +0.8$ V, $E^\circ_{Mg^{2+}/Mg} = -2.37$ V. What will be the effect of E.M.F. if concentration of Mg^{2+} is decreased to 0.1 M ?

(*c*) Explain the following characteristics of transition metals :

(*i*) Tendency to form complexes,

(*ii*) Tendency to exhibit variable oxidation states,

(*iii*) Catalytic behaviour. 3×3

8. (*a*) Why is freezing point of H_2O lowered on adding NaCl whereas its boiling point is elevated ? How are these properties used for determining molecular weights ?

(*b*) Describe the trends in the following properties of group 17 elements :

(*i*) Metallic character

(*ii*) Acidic character of their oxides

(*iii*) Catenation

(*iv*) Stability and acidic/basic character of their hydrides. 5×2

PAPER II

Time allowed : 3 hours *Maximum marks : 70*

General Instructions : *Attempt all questions.*

1. (*a*) Why are bond orders of He_2^+ and H_2^- identical ?

(*b*) Which of these two, $CdCl_2$ and NaCl, will produce Schottky defect, if added to a AgCl crystal ?

(*c*) Why is OF_6 compound not known ?

(*d*) Complete the nuclear reaction given below :

$$^{27}_{14}Si \rightarrow {}^{27}_{13}Al + \cdots\cdots$$

(e) What is galvanisation of iron ?

(f) Why is platinum (IV) state more stable than nickel (IV) state ?

(g) Write all the isomers of $[Co(NH_3)_6][Cr(C_2O_4)_3]$.

(h) Give the importance of vitamin C.

(i) Write the names of two narcotics which are used as analgesics.

(j) What are disperse dyes ? 1×10

2. (a) In the hydrogen atom the energy of the electron in first Bohr's orbit is $-13{\cdot}12 \times 10^5$ J mol^{-1}. What is the energy required for its excitation to second Bohr's orbit ?

(b) A solid A^+B^- has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation ? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal A^+B^- ? Give reason for your answer.

(c) The reaction $C_2H_5I \rightarrow C_2H_4 + HI$ is of first order and its rate constants are $3{\cdot}20 \times 10^{-4}$ s^{-1} at 600 K and $1{\cdot}60 \times 10^{-2}$ s^{-1} at 1200 K. Calculate the energy of activation for the reaction. (Given R=8.3 J K^{-1} mol^{-1}).

(d) What is the order of a chemical reaction ? How will you prove that a chemical reaction is of first order or not ? 2×4

3. (a) Dissociation energy of H_2 (g) and Cl_2 (g) are respectively 435·4 and 243 kJ mol^{-1}. Enthalpy of formation for HCl (g) is $-92{\cdot}2$ kJ mol^{-1}. Calculate the dissociation energy for HCl.

(b) Radio isotope $^{32}_{15}P$ has a half life of 15 days. Calculate the time in which the radioactivity of its 1 mg quantity will fall to 10% of the initial value.

(c) What are the differences between hydrophobic and hydrophilic sols ?

(d) Explain the geometry of $[Cr(NH_3)_6]^{3+}$ ion by valence bond theory of complexes. Why is this ion NOT diamagnetic ? (Atomic number of Cr=24) 2×4

4. (a) How will you obtain phenol from benzene and convert it into 4-bromophenol ?

(*b*) Write IUPAC name of diethyl ether. How will you obtain it from ethanol ?

(*c*) Complete the following reactions :

$AgCl + CH_3NH_2 \rightarrow$

$CHCl_3 + CH_3NH_2 + KOH \rightarrow$

(*d*) How its terylene synthesized ? What type of polymer it is ? 2×4

5. (*a*) Explain the terms 'micelles' and 'emulsions'. 'Action of soap is due to emulsification and micelle formation'—Comment.

(*b*) Size of trivalent lanthanide cation decreases with increase in the atomic number. Explain.

(c) Explain the functions of nucleic acids.

(*d*) Write structure of ATP. Why is ATP an energy-rich molecule ? 2×4

6. (*a*) How will you obtain chlorobenzene, aniline and salicylic acid from benzene ?

(*b*) Why is chloroacetic acid a stronger acid than acetic acid ? How will you obtain acetic acid from methanol ? How may acetic acid be converted into ethane ?

(*c*) What happens when,

(*i*) an alkyl halide reacts with $AgNO_2$ and the product is reduced.

(*ii*) ethyl amine reacts with excess of methyl iodide.

(*iii*) aniline is diazotized and the product is reacted with phenol. 3×3

7. (*a*) What is second law of thermodynamics ? For spontaneity of the process explain the thermodynamic criteria. The ΔH and ΔS for $2Ag_2O\ (s) \rightarrow 4Ag\ (s) + O_2\ (g)$ are +61.17 kJ mol^{-1} and +132 J K^{-1} mol^{-1} respectively. Above what temperature will the reaction be spontaneous ?

(*b*) Calculate the E.M.F. of the cell

$Mg\ (s)\ |\ Mg^{2+}\ (0.1\ M)\ \|\ Ag^{+}\ (1 \times 10^{-4}\ M)\ |\ Ag$

$E^{\circ}_{Ag^{+}/Ag} = 0.8\ V,\ E^{\circ}_{Mg^{2+}/Mg} = -2{\cdot}37\ V.$

What will be the effect on E.M.F., if concentration of Ag^{+} is increased to 1×10^{-3} M ?

(*c*) Explain the following properties for transition elements :

(*i*) Metallic character

(*ii*) Tendency to form complexes

(*iii*) Magnetic behaviour 3×3

8 (*a*) What is osmotic pressure ? Why is osmotic pressure measurement better than the elevation in boiling point method for determination of molecular weights ? The osmotic pressure of a solution containing 1.0 g protein in 200 ml of aqueous solution at 27°C has been found to be $2 \cdot 0 \times 10^{-3}$ atm. Calculate the molecular mass of protein (R=0.082 L −atm −mol^{-1} K^{-1}).

(*b*) Describe the trends in the following properties of group 17 elements :

(*i*) Non-metallic character

(*ii*) Acidic character of their oxides

(*iii*) Catenation

(*iv*) Stability and acidic character of their hydrides. 5×2

PAPER III

Time allowed : *3 hours* *Maximum marks* : *70*

Note : *Attempt all questions.*

1. (*a*) Why is acetylene molecule linear ?

(*b*) What is the number of oxygen atoms shared between Si atoms in $Si_3O_9^{6-}$ ion ?

(*c*) Why does beryllium resemble aluminium in its chemical properties ?

(*d*) Complete the nuclear reaction $^{14}_{7}N\,(\alpha, ?)\,^{18}_{10}Ne$.

(*e*) To deposit 1 mole of aluminium from an aqueous solution of $Al_2(SO_4)_3$, what is the amount of electricity (in Coulombs) required ?

(*f*) Which is the trivalent ion having the largest size in the lanthanide series ?

(*g*) Write all the isomers of $[Co(NH_3)_5NO_2]\ Cl_2$.

(*h*) What are the constituent units of cellulose ?

(*i*) Explain with an example, the term mordant dyes.

(*j*) Why is bithional added to soap ? 1×10

2. (*a*) Write the four quantum numbers of the outermost two electrons of Ca (atomic no. of Ca is 20).

(*b*) An element 'A' crystallizes in f.c.c. structure. 208 g of it has $4 \cdot 2832 \times 10^{24}$ atoms. Calculate the edge of the unit cell if density of 'A' is $7 \cdot 2$ g/cm^3.

(*c*) Define activation energy. How is it related to the rate constant of the reaction ?

(*d*) A reaction that is of the first order with respect to reactant 'X' has a rate constant 6 min^{-1}. If we start with [X]=5 mol L^{-1}, when would [X] reach the value 0·05 mol L^{-1} ? [log 5=0.6990] 2×4

3. (*a*) Calculate the equilibrium constant at 25°C for $H_2+I_2 \rightleftharpoons 2HI$, if standard free energy of formation for HI is 1·30 kJ mol^{-1}. [R=8·31 JK^{-1} mol^{-1}]

(*b*) Write whether the following are nuclear fusion or nuclear fission reactions :

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{140}_{56}Ba + {}^{93}_{36}Kr + 3\,{}^{1}_{0}n$$

$$^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{4}_{2}He$$

In which of them energy released is higher ?

(*c*) Explain the terms 'micelle' and 'emulsion'.

(*d*) Using valence bond theory explain the diamagnetic nature and square planar structure of $[Ni(CN)_4]^{2-}$ ion. (Atomic no. of Ni is 28) 2×4

4. (*a*) How will you convert
   (*i*) aniline to chlorobenzene and
   (*ii*) chlorobenzene to salicylaldehyde ?

(*b*) How will you obtain aldol from acetaldehyde ?

(*c*) Write the IUPAC name of dimethylamine. How will you obtain it from nitromethane ?

(*d*) Explain addition and condensation polymers by giving one example in each case. 2×4

5. (*a*) List the main differences between physical and chemical adsorption, and depict graphically the variation of extent of adsorption with temperature at constant pressure for both types of adsorption.

(*b*) Predict with justification the number of moles of KI that would be oxidized by acidified aqueous solutions of
   (*i*) 1 mole of $K_2Cr_2O_7$
   (*ii*) 1 mole of $KMnO_4$

(*c*) Explain primary and secondary structures of proteins.

(*d*) Write the functions of steroid and peptide hormones. 2×4

6. (*a*) Write IUPAC name of iso-propyl bromide. How is it synthesized from propylene and converted to 2-propanone ?

(*b*) Why is pKa value for chloroacetic acid lower than that of acetic acid ? How can we obtain methane and acetic anhydride from acetic acid ?

(*c*) CH_3OH and CH_3NH_2 have nearly the same molecular mass but differ by 68 K in b. pts. Explain. Why is methyl amine a stronger base than ammonia ? Write the reaction of methyl amine with $CHCl_3$ and KOH. 3×3

7. (*a*) State third law of thermodynamics. The standard absolute entropies of HCl (g), H_2 (g) and Cl_2 (g) at 298 K are 187·7, 130·6 and 223 JK^{-1} mol^{-1} respectively. Calculate the entropy change in the formation of HCl (g) from H_2 (g) and Cl_2 (g).

(*b*) Write the Nernst equation for the potential of the cell $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$. How can equilibrium constant for the reaction of this cell be estimated from the cell potential ? Predict the effect of temperature on the equilibrium constant.

(*c*) (*i*) Why do ionic radii decrease in the order Ti^{2+}, V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ?

(*ii*) Who do transition elements from coloured compounds.

3×3

8. (*a*) What is Raoult's Law ? How is it formulated for a solution of a non-volatile solute ? Why does the law not hold for the chloroform-acetone and the cyclohexane-ethanol mixtures ? Describe the nature of deviation and its reason for each mixture.

(*b*) Describe the trends in the following properties of group 16 elements :

(*i*) Metallic character

(*ii*) Catenation

(*iii*) Stability of the hydrides

(*iv*) Capability to form halides

(*v*) Acidic character of the oxides. 5×2

□□

WHY THIS BOOK ?

— To offer better exposition of the subject matter.

— To equip the students with all informations and methods for an excellent performance in their examinations.

— To help the students of all levels.

— To make the study of Chemistry an active and visual experience.

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Also Extreme[illegible] [illegible]r

* Self-studying and revising [illegible] matter.

* Preparing for Class XII exam[illegible] and for competitive entrance examinations, such as IIT - JEE, PMT, etc.,

* Understanding the meanings of words, terms etc.

* Class discussions

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About the Author

D.P. Goel has been teaching Chemistry at St. Stephen's College, University of Delhi for the past 20 years. Besides having actively participated in several NCERT Workshops (spanning the teaching of Chemistry at school level), he has been associated with the preparation of model curriculum, textual and other supporting materials in Chemistry for different study levels. He has written a number of books on Chemistry and co-authored **'Pathways of Chemistry'** for Class XI which has been recommended by the C.B.S.E.